SYNTHETIC AND MECHANISTIC INVESTIGATIONS OF ORGANOPLATINUM CHEMISTRY

THESIS

submitted to the

UNIVERSITY OF GLASGOW

in fulfilment of the

requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

IAN G. PHILLIPS B.Sc.

Department of Chemistry

University of Glasgow

October 1981

Acknowledgements

For his advice, encouragement and friendship throughout the course of this research I heartily thank my supervisor, Dr. Ronald J. Cross. I should also like to thank Dr. D.S. Rycroft for his help in recording n.m.r. spectra, and for helpful discussions in their interpretation. Thanks are also due to Dr. A.G. Lappin for kinetic measurements.

I wish to express my gratitude to Miss Aileen Frew, Drs. Lj.Manojlovic-Muir and K.W. Muir for an X-ray structural determination, and to Mrs. F. Lawrie and her assistants for the recording of infrared spectra.

The award of a research studentship by the Science Research Council is gratefully acknowledged.

Abstract

The addition of PMe_2Ph to $[Pt_2Cl_4(PMe_2Ph)_2]$ at low temperatures produces the ions $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2Ph)]^-$ as major products, as well as some of the expected $[PtCl_2(PMe_2Ph)_2]$. Less ionic material is produced from the addition of PBu_3 to $[Pt_2Cl_4(PMe_2Ph)_2]$ and PMe_2Ph to $[Pt_2Cl_4(PBu_3)_2]$, and none at all from the addition of PBu_3 to $[Pt_2Cl_4(PBu_3)_2]$. Ionic materials are also produced in the reactions of $PMePh_2$ and $SPMePh_2$ with $[Pt_2Cl_4(PBu_3)_2]$, and of PBu_3 and $SPBu_3$ with $[Pt_2Cl_4(PMePh_2)_2]$. The nature of the neutral ligands involved has a profound effect on the course of the reactions.

The ionic materials undergo rapid phosphine exchange even at -60°C if excess ligand (R_3P or Cl^-) is present and they complicate the range of products observed unless steps are taken to prevent local accumulations of free ligand in the course of mixing the reactants. The novel mechanism of asymmetric bridge cleavage by monodentate ligands is discussed. $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2Ph)]^-$ (1:1) convert to a 1:1 cis/trans $[PtCl_2(PMe_2Ph)_2]$ mixture upon warming to room temperature.

The bridge cleavage of cis/trans-$[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ by CO at -60°C to give almost exclusively $[PtClPh(CO)(PMePh_2)]$ {P trans to CO, isomer III} is investigated from the point of view of an asymmetric bridge cleavage mechanism. However, the expected intermediates, cis-$[PtPh(CO)_2(PMePh_2)]^+$ and cis$[PtCl_2Ph(PMePh_2)]^-$, give isomer II $[PtClPh(CO)(PMePh_2)]$ {P trans to Cl} and III as they lose or gain CO respectively at -60°C, and another mechanism must be sought.

Cis-$[PtCl_2\{P(p\text{-tolyl})_3\}_2]$ reacts with CO and sulphur in $CHCl_3$ at 20°C to give $(p\text{-tolyl})_3PS$ and cis-$[PtCl_2(CO)\{P(p\text{-tolyl})_3\}]$ in two hours. A wide range of cis and trans $[PtX_2L_2]$ give similar products but to a lesser extent. The ionic species cis and trans-$[PtX(CO)L_2]X$ are proposed as important intermediates in the carbonylation process, and the reactions of these cations with halide and sulphur are examined. An overall carbonylation scheme is discussed.

The reactions of a smaller range of $[PtX_2L_2]$ with CNPh and sulphur give similar products: cis-$[PtX_2(CNR)L]$ and LS. The same products result from the treatment of trans-$[PtCl(CNR)L_2]Cl$ with sulphur at +20°C. These ionic complexes are proposed as important intermediates in the isonitrile reaction, which has very similar characteristics to the carbonylation process. An analogous mechanistic scheme is discussed.

$CDCl_3$ solutions of cis-$[PtCl_2L_2]$ react with $AgSO_3CF_3$ at room temperature to give $[Pt_2(\mu\text{-}Cl)_2L_4](SO_3CF_3)_2$ and solvent assisted exchange of halide between the dimers and cis-$[PtCl_2L_2]$ is observed. This exchange is rapid at +30°C but much slower at -60°C, and in the absence of free halide.

The reactions of cis-$[PtCl_2(CNR)L]$ with isonitrile and of cis-$[PtCl_2(CNR)_2]$ with tertiary phosphine (L) are complicated. Broad phosphorus resonances are noted which persist for several weeks until the isonitrile is lost (CNMe) or decomposes (CNPh).

Cis-$[PtCl_2(CNR)L]$ {R = Me L = $PMePh_2$, R = Ph L = $PMePh_2$, PMe_2Ph, PBu_3} are the products of the addition of CNR to $[Pt_2Cl_4L_2]$ at room tem-

perature. At -60°C trans-$[PtCl_2(CNPh)(PMe_2Ph)]$ is produced from the reaction of CNPh and $[Pt_2Cl_4(PMe_2Ph)_2]$, and it isomerises upon warming. Trans-$[PtCl_2(CNPh)(PMePh_2)]$ is produced from the addition of CNPh to $[PtCl_3(PMePh_2)]^-$ at -60°C. If the isonitrile is added neat however, inhomogenous mixing results in the appearance of many unexpected products, including cis and trans $[PtCl_2L_2]$ and trans-$[PtCl(CNR)L_2]^+$.

All three possible isomers of $[PtClPh(CNPh)(PMePh_2)]$ are produced in the reaction of $[PtCl_2Ph(PMePh_2)]^-$ with CNPh at -60°C. On warming, isomer I (P trans to Ph) inserts to give cis-$[Et_4N][PtCl_2(C\{Ph\}=NPh)(PMePh_2)]$ whilst II (P trans to Cl) and III (P trans to CNPh) remain unchanged. The analogous CO reaction produces $[PtClPh(CO)(PMePh_2)]$ (P trans to CO) only. Isomers II and III are the products of bridge cleavage of $[Pt_2Cl_2Ph_2(PMePh_2)_2]$ by CNPh at -60°C if a tangential mixing apparatus is employed. If neat CNPh (or CNMe) is added to the dimer other products result, including trans-$[PtClPh(PMePh_2)_2]$, trans-$[PtPh(CNPh)(PMePh_2)_2]^+$ and the uncommon asymmetrically substituted dimeric complexes $[Pt_2(\mu\text{-}Cl)_2Cl(C\{R'\}=NR)(PMePh_2)_2]$.

Cis-$[PtCl_2(CNR)L]$ react with bis alkyl and aryl mercurials to give isomer II complexes and the asymmetrically substituted dimers. After several days, decomposition to cis-$[PtCl_2(PMePh_2)]$ is noted.

When treated with CO, cis-$[PtClPhL_2]$ are converted to the trans isomers without incorporation at +20°C. At -60°C, isomer I $[PtClPh(CO)L]$ {L trans to Ph} is produced and the displaced phosphine appears as $[PtPhL_3]^+Cl^-$ (L = $PMePh_2$) whilst the Ph_3P equivalent of

this complex has not been unambiguously assigned. These complexes are formed from the reaction of cis-$[PtClPhL_2]$ with phosphine (L), which has a comparable rate to the reaction of isomer I with L, but is faster than the oxidation of L. At room temperature $[PtPh(PMePh_2)_3]Cl$ is in equilibrium with trans-$[PtClPh(PMePh_2)_2]$ in $CDCl_3$ solution.

Cis-$[PtClPhL_2]$ reacts with $AgSO_3CF_3$ and CO at -60°C to give isomer I, $[PtPhL_3]SO_3CF_3$ and cis-$[PtPh(CO)L_2]SO_3CF_3$. The latter complex inserts cleanly on warming to room temperature to produce, eventually, trans-$[Pt(COPh)(CO)L_2]SO_3CF_3$. The isomer I complexes $[PtClR'(CO)L]$ {P trans to R} reacts with tertiary phosphine to give products from CO loss at -60°C, insertion at room temperature and variable amounts of both products at intermediate temperatures. The isomer I complexes $[PtCl(Y\text{-}C_6H_4)(CO)(PMePh_2)]$ {Y = CN, Cl, H, MeO_2C-, all p} react with Cl^- to give cis-$[PtCl_2(COC_6H_4Y)(PMePh_2)]^-$.

Cis-$[PtClPh(PMePh_2)_2]$ reacts with $AgSO_3CF_3$ and CNPh to give cis-$[PtPh(CNPh)L_2]SO_3CF_3$, $[PtClPh(CNPh)(PMePh_2)]$ {P trans to Ph}, $[PtPh(PMePh_2)_3]SO_3CF_3$ and two unknown cis complexes at -60°C. Upon warming to +30°C the cis complexes isomerise slowly, isomer I inserts and trans-$[Pt(C\{Ph\}=NPh)(CNPh)(PMePh_2)_2]SO_3CF_3$ is detected. CNMe and CNPh react with trans-$[PtClPh(PMePh_2)_2]$ to give trans-$[PtPh(CNR)(PMePh_2)_2]Cl$, the CNMe analogue of which is unchanged after several weeks. The CNPh complex converts, via an intermediate assigned as cis-$[PtCl(C\{Ph\}=NPh)(PMePh_2)_2]$ to trans-$[PtCl(C\{Ph\}=NPh)(PMePh_2)_2]$ Much less cis species is produced in the presence of $AgSO_3CF_3$ and S_8.

The reactions of [PtClPh(dpe)] with CO and CNR (and $AgSO_3CF_3$) are investigated and their implications on a general reaction mechanism are discussed.

CONTENTS

Page

CHAPTER ONE

Chapter 1 - Introduction

Soon after its arrival in Europe in 1741 a systematic study of the chemistry of platinum began. By 1830 not only had many of its inorganic compounds been made but the first organometallic derivative $K.[PtCl_3(C_2H_4)]H_2O$[1] had actually been prepared. It is now known that this complex, called Zeise's salt after the chemist who prepared it, contains a platinum-olefin bond, but when it was first isolated its structure was unknown. The zinc alkyls prepared nearly twenty years later by Frankland[2] when he was investigating the 'ethyl-radical' are perhaps the first organometallic species characterised as such. Shortly after this pioneering work ethyl-complexes of lead, tin and mercury were prepared by Buckton[3] using diethyl-zinc, another compound that Frankland characterised.

In 1900 Grignard reported his investigations of methyl-magnesium iodide,[4] a complex whose wide ranging organometallic synthetic applicability was later demonstrated convincingly by Pope and Peachey[5] in their preparations of methyl-compounds of the Group VIII metals. The most notable complexes prepared by these workers were the very stable trimethyl platinum derivatives. In later years the versatility of alkali-metal alkyl complexes in organic synthesis[6,7] made possible the preparation of previously unobtainable organic compounds. Ziegler and Colonius[7] observed the reaction of butyl-lithium and excess liquid mercury to give bis-butylmercury after two days.

The first simple complexes in which monodentate organic groups were bound to platinum(II) by a metal-carbon sigma-bond were reported by Chatt and Shaw[8] in 1959. They are of the types $[PtR_2(PR_3)_2]$ and $[PtX\ R(PR_3)_2]$ {R = alkyl, PR_3 = tertiary phosphine and X = halide or pseudohalide}. Three years later the same authors also prepared several hydrido platinum compounds with phosphine and arsine ligands.[9] For some time it was thought that the phosphine and arsine ligands which these complexes contained were essential to their stability because the π-acceptor and σ-donor capacities of these ligands modified the metal-d orbitals and made metal-carbon σ-bond formation possible. Although to some extent this is true, it is possible to prepare σ-bonded organoplatinum complexes without these particular ligands but instead containing ligands such as acetylacetonate[10], norbornadiene[11], cyclooctadiene[11], pyridines[11] or stibines[12].

Today many challenging questions and objectives, both of a scientific and practical nature, are associated with those heterogeneously and homogeneously catalysed reactions involving the transition metals and their complexes. These range from Wilkinson's complex $[Rh\ Cl\ (PPh_3)_3]$ catalysed hydrogenation of olefins[13], the hydroformylation of olefins (the OXO process), and the palladium chloride catalysed oxidation of olefins, to rhodium catalysed carbonylation of methanol, and the Ziegler Natta polymerisation of olefins by alkyl $TiCl_3$ complexes. Also of vital importance are those processes which facilitate the reaction of unactivated organic centres[14].

The metal sites in these processes serve to 'choreograph' the reactions of highly reactive species like H^- and CH_3^- by acting as assembly points to make them accessible reaction intermediates. The total number of valence electrons in these intermediate complexes is a critically important factor of these specifically directed reactions.

The 16-18 Electron Rule

The tendancy for transition metals to form complexes in which the metal has an effective atomic number equivalent to the next higher noble gas has long been recognised.[15] To achieve this stable electronic configuration the metal must fill all of its valence orbitals, bonding and nonbonding, but not its antibonding orbitals. Increasing atomic weight and nuclear charge, however, decrease the d-orbital energies and in turn raise the nd—(n+1)p electronic promotion energies, making a full 18-electron configuration difficult to achieve. Accordingly the Group VIII metals commonly form 16-electron species e.g. $[PtX_2L_2]$ X = halide or pseudohalide, L = two electron neutral donor ligand[16], and at the extreme right hand end of the periodic table 14-electron compounds are typical, such as $[AuMe(PPh_3)]$.[17]

Descending a group the nd—(n+1)p promotion energies vary irregularly[18] because of the lanthanide contraction, and it is found that second row metals like Pd and Rh tend to form stable 16-electron complexes[19] whilst Ir and Pt favour both 16- and 18- electron compounds.[20]

The ligands surrounding the metal influence the attainment of the 18-electron configuration greatly. The formally five-electron donor cyclopentadienyl ligand is known to stablise 18-electron complexes of Pd^{II} [21] although the metal on the whole favours a 16-electron configuration.

In 1972 Tolman formulated the '16-18 Electron Rule'[22] and showed that it was consistent with the large body of experimental evidence, including studies on reaction mechanisms, in organometallic chemistry and homogeneous catalysis. The rule states that diamagnetic organometallic complexes of transition metals may exist in a significant concentration at moderate temperatures only if the metal's valence shell contains 16 or 18 electrons, and also that the reactions of these complexes proceed by elementary steps involving 16 or 18 electron intermediates, (equations 1[23] and 2[22]).

$$\underset{18}{[MeMn(CO)_5]} \longrightarrow \underset{16}{[(MeCO)Mn(CO)_4]} \xrightarrow{CO} \underset{18}{[(MeCO)Mn(CO)_5]} \qquad (1)$$

$$\underset{18}{[Ni(CO)_4]} \xrightarrow{-CO} \underset{16}{[Ni(CO)_3]} \xrightarrow{PPh_3} \underset{18}{[Ni(CO)_3(PPh_3)]} \qquad (2)$$

Although the first part of the rule restates what is universally accepted the second aspect outlines how the particular number of valence electrons limits the choice of reactions available to a complex. Reactions which involve the metal directly can therefore be broken down into five elementary processes, and their reverse: Lewis acid dissociation (equation 3): Lewis base dissociation (equation 4): reductive elimination (equation 5); insertion (equation 6) and oxidative coupling (equation 7).

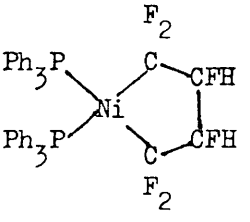
$$\underset{18}{\left[CpRh(C_2H_4)_2SO_2\right]} \longrightarrow SO_2 + \underset{16}{\left[CpRh(C_2H_4)_2\right]} \quad (3)$$

$$\underline{trans}\underset{16}{\left[PtClR(PEt_3)_2\right]} \xrightarrow{py} \underset{18}{\left[PtClRpy(PEt_3)_2\right]} \longrightarrow \underline{trans}\underset{16}{\left[PtRpyL_2\right]}Cl \quad (4)$$

$$\underset{18}{\left[IrH_2(CO)_2\{P(C_6H_{11})_3\}_2\right]^+} \xrightarrow{H_2} \underset{16}{\left[Ir(CO)_2(P\,Cy_3)_2\right]^+} \xrightarrow{CO} \underset{18}{\left[Ir(CO)_3(PCy_3)_2\right]^+} \quad (5)$$

$$\underset{16}{\left[PtClH(PEt_3)_2\right]} \xrightarrow{C_2H_4} \underset{18}{\left[PtClH(C_2H_4)(PEt_3)_2\right]} \longrightarrow \underset{16}{\left[PtClC_2H_5(PEt_3)_2\right]} \quad (6)$$

$$\left[Ni(C_2H_4)(PPh_3)_2\right] + 2CF_2CFH \longrightarrow \quad (7)$$



Platinum and Palladium Complexes

Platinum and palladium complexes are known with the metals formally zero-, di- and tetravelent. Evidence so far of uni- and trivalent compounds is not definitive and only platinum is known to form complexes in the +5 and +6 oxidation states[24].

Of the various zerovalent complexes, those containing tertiary phosphine ligands have been the most widely investigated largely because of their stability[25]. Only palladium is known to form zerovalent isonitrile complexes which have the general formula $\left[Pd(CNR)_2\right]$. These compounds are the only known case of formerly coordinatively unsaturated isocyanide complexes.[26] The teriary-phosphine complexes have coordination numbers from four to two and the tetracorordinate species react generally by first dissociating the give the tris- and then the bis-phosphine complexes. The bis-phosphine complexes

in turn may react via an oxidative addition (and a consequent change in oxidation state), or purely additively with another molecule to give another zerovalent complex[26]. (equations 8[27] and 9[28])

$$[Pd(PPh_3)_4] + 3I_2 \longrightarrow [Pd^{II}I_2(PPh_3)_2] + 2Ph_3PI_2 \quad (8)$$

$$[Pt(PPh_3)_4] + C_2(CN)_4 \longrightarrow [Pt\{C_2(CN)_4\}(PPh_3)_2] + 2PPh_3 \quad (9)$$

The latter type of reaction (equation 9) is reserved for ligands having low lying antibonding orbitals capable of delocalising the negative charge on the metal, by a π-back bonding mechanism, such as olefins, acetylenes or carbon monoxide.

Much interest has centred around the study of the reactions of the zerovalent metals, particularly those involving no overall change in oxidation state, because the metal sites in these complexes may closely resemble the sites in chemisorbed bulk metal clusters during heterogeneous catalysis. The oxygen adducts of the zerovalent metals of Ni, Pd and Pt catalyse the oxidation of phosphine to phosphine oxide and of isonitrile to to isocyanate.[29]

Complexes of the metals in the +4 oxidation state are known but there are fewer palladium (IV) than platinum (IV) complexes largely because of the much higher ionisation energy needed to produce Pd^{4+} than Pt^{4+}. Most of the tetravalent complexes of platinum have octahedral structures (or nearly so) and they are diamagnetic. Among the very few PdIV complexes known are $[Pd(NH_3)_nCl_{6-n}]^{m+}\{n=1.2\}$ trans-$[PdCl_2(C_6F_5)_2(PPh_3)_2]$[30] and the binary chalcogenides.[31] Platimum forms tetravelent complexes with ligands containing most of the

principal donor atoms in the periodic table except for elements of Groups I, II and III. Organometallic complexes of PtIV are conveniently prepared by the addition of an organo-halide to the corresponding platinum II complex.

Far and away the most extensively studied complexes of platinum and palladium are those in which the metal is formally in the +2 oxidation state. They are most commonly tetracoordinate and square planar. With eight d-electrons, it is possible for the metals to leave the $d(x^2-y^2)$ orbital vacant and attain this geometry. Other stereochemistries with higher coordination numbers are known but they are less common[24]. Most of the divalent metal complexes studied today contain coordinated N, P or As donor ligands in their coordination spheres.

Hartley has reviewed the preparation of a wide range of useful starting materials of both the zero- and divalent metals which are commonly encountered in a diverse range of preparative routes[33]. Amongst these are included the bis-(benzonitrile)-, bis-(olefin)-, and bis-(tertiary phosphine)- metal II dihalides, and perhaps most important of all the halide-bridged bis-tertiary phosphine dimeric complexes. These latter compounds have provided the basis for the preparation of a vast collection of monomeric divalent metal complexes by the application of bridge cleavage reactions ever since their first prepareation[34], (for example equations 10[35] and 11[36]).

$$[Pt_2Cl_4(PPh_3)_2] \xrightarrow{CO} 2\underline{cis}\,[PtCl_2(CO)(PPh_3)] \qquad (10)$$

$$[Pt_2Cl_4(PEt_3)_2] \xrightarrow{2PhNC} 2\underline{cis}\,[PtCl_2(CNPh)(PEt_3)] \rightarrow 2\underline{cis}\,[PtCl_2(CO)(PPh_3)] \qquad (11)$$

The organometallic chemistry of the metals in their divalent states are characterised by the many different types of metal-organic fragment linkages. The simplest type is the metal-carbon σ-bond of metal alkyl and aryl complexes. The platimum II σ-bonded organometallics are reasonably stable with respect to thermal, oxidative and solvolytic factors whilst the palladium II complexes are less so. For example whilst cis-$[PtMe_2(PEt_3)_2]$ may be vacuum distilled at ca 85°C [8] the analogous triphenyl-phosphine palladium complex decomposes in solution just above room temperature[37]. Surprisingly the bond energy of a typical metal-carbon σ-bond (the aryl carbon-Pt bond in $[PtPh_2(PEt_3)_2]$) at a minimum energy of 250kJmol^{-1},[38] whilst being a strong bond, is far less than the energy associated with the carbon-carbon and carbon-hydrogen bonds in the organic compounds which are the main products of thermal decomposition. It appears that the stability of platimum-carbon σ-bonds must be of a kinetic and not a thermodynamic origin.

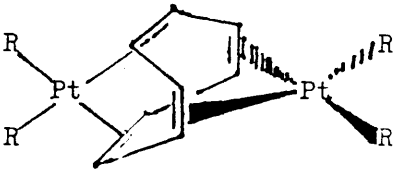
In the divalent metal carbonyl and isonitrile complexes the ligands are both σ-bonded to some extent but π^* antibonding orbitals on these ligands receive charge from the metal orbtials by a π-retroactive mechanism. Accordingly, in these cases, the metal carbon bonds are shorter than typical metal-alkyl or -aryl bonds.[39,40,41] The extent of π-back bonding in the metal alkyl and aryl complexes is somewhat uncertain[42], but in general metal-aryl bonds tend to be shorter and stronger than metal alkyl bonds, and aryl complexes are, on the whole, more stable with respect to decomposition. Carbene complexes are another case where the metal carbon linkages have bond orders greater than one.

In both the zero- and divalent states platinum and palladium form a diverse range of olefin and acetylene complexes. Chatt et al described the bonding of olefins in 1953[44]. The olefin donates π-charge density to vacant metal σ-bonding orbitals, of the correct symmetry for overlap, causing a disfavourable negative charge on the metal. This is alleviated through synergic back donation of charge the the olefin π^*-antibonding orbitals, and the resultant decrease in bond order is seen as a decrease in the olefin stretching frequency. The olefins lie perpendicular to the plane of the metal and the other ligands in the solid state, but have large amplitudes of rotation in solution.[46] Acetylenes bond in an analogous manner[47], but form stronger bonds to the metal.[48]

The di-olefin chelate ligands (1.5) cycloactadiene norbornadiene and dicyclopentadiene form complexes of great synthetic utility.[49,50] Whilst they are easily displaced by phosphine or arsine, they may remain either wholly or partially ligated during the substitution of other groups coordinated to the metal[51] (equation 12) (L = tertiary phosphine, R = Ph).

$$[PtCl_2(1.5\text{-cod})] \xrightarrow[RHgCl]{R_2Hg} [PtClR(1,5\text{-cod})] \xrightarrow[-cod]{2L} \underline{trans}\text{-}[PtClRL_2] \qquad (12)$$

Other organic groups formerly donating more than a lone pair of electrons are known, including π-allyls[52], cyclobutadiene [53], cyclotentadiene [54], and the mixed σ and π bonded ligands such as methoxydicyclopentadiene [50]. Cyclooactatetraene bridges the two metals in the complexes $[Pt_2R_4(C_8H_8)]$[55] where R = Me, Ph



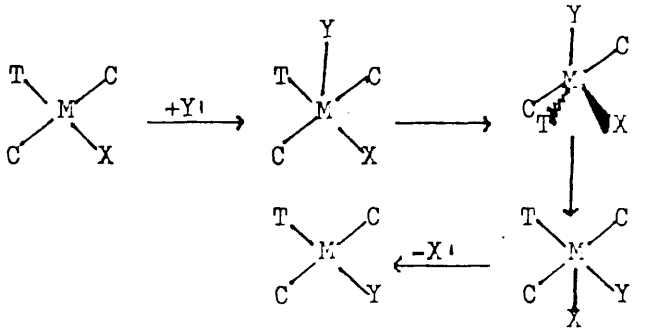
Metallacyclic complexes of platinum[56] and palladium are known. Palladium metallacyclobutadienes are implicated in the heterogeneously catalysed cyclotrimerisation of acetylenes[58] whilst a platinacyclobutane is formed in the thermal decomposition of cis-$[Pt(neo\text{-}pentyl)_2(PEt_3)_2]$[57]. Studies of the isomerisation of substituted platinacyclobutanes question ideas about the stabilities of intermediates in the olefin metathesis reaction, and provide an explanation for degenerate olefin metathesis[59].

Finally, the metals and their complexes catalyse a diverse range of processes, including light induced hydrogen evolution from water (catalysed by platinum metal colloidal hydrosols)[60], stereospecific sigmatropic rearrangements of allylic acetates by $[PdCl_2(CH_3CN)_2]$ in prostaglandin synthesis[61], the Pd catalysed carbonylation of halo-alcohols in lactone synthesis[62], the dimerisation of ethylene catalysed by $[PdCl_2(C_2H_4)_2]$[63] and in organic syntheses.[64]

Selected Reaction Mechanisms in Transition Metal Chemistry:

Nucleophilic Substitutions

Nucleophilic substitutions in platinum (II) chemistry are generally associative. Displacement of ligands proceeds by bimolecular attack of solvent or nucleophile, through the formation of a trigonal bipyramidal 5-coordinate intermediate, with complete retention of configuration.[65] Scheme I .



SCHEME I

The most important factor governing the site of substitution is the 'trans-effect' of T (i.e. the ability of T to labilise leaving group X). The trans-effect of a coordinated ligand is the effect of that ligand on the rate of substitution trans to it in a metal complex,[66] and it is a phenomenon apparent from both kinetic and preparative[67] studies. It was noted in 1926 by Chernyaev.[67] A series of ligands arranged qualitatively in order of decreasing trans- effect [68] is:

$CO, CN^-, C_2H_4 > PR_3, H^- > CH_3^-$, thiourea $> NO_2, I, SCN\ Br > Cl > py, NH_3 > H_2O, CH_3OH$.

Two explanations have arisen to account for the observed kinetic results, a polarisation theory and a π-bonding theory. The first theory emphasises bond weakening trans to a ligand by charge polarisation and σ-bonding effects, whilst the second considers convalent π-bonding and how it can stablise the trigonalbipyramidal transition state of a bimolecular displacement reaction. The first theory is adequate in describing the high trans- effects observed for H^-, CH_3^- and $C_6H_5^-$ where one expects both strong polarisation and σ-bonding.[68] The π-bonding theory was suggested by Chatt and coworkers [69] in 1955 and later by Orgel.[70] Chatt argued that a π-acceptor ligand like R_3P, CO or C_2H_4, in removing charge from the metal, favoured the addition of the incoming ligand Y to form a 5 coordinate transition state. Orgel stressed that the increased stability of this species resulted from a removal of electron density along the Pt-X and Pt-Y directions, thus weakening these bonds. Both σ and π contributions to a ligand's overall trans-effect require careful consideration when interpreting kinetic data.

In 1966 the term trans-influence[71] was proposed to describe the purely ground state bond weakening phenomena noted from X-ray structural determinations, and in some cases from spectroscopic measurements. An approximate series of ligands arranged according to decreasing trans-influence (from structural data) are as follows:[72]

$R_3Si \sim \delta\text{-}C \sim H^- \geq$ carbene $\sim PR_3 \geqslant AsR_3 > CO \sim CNR \sim C=C \sim Cl^- \sim NH_3 > O(acac)$

This sequence is not the same as that obtained for the trans-effect with the most obvious discrepancy occuring in the case of ethylene. Although it has a high trans-effect the M-Cl bond length trans to ethylene in complexes such as Zeise's salt are not abnormally short.[72]

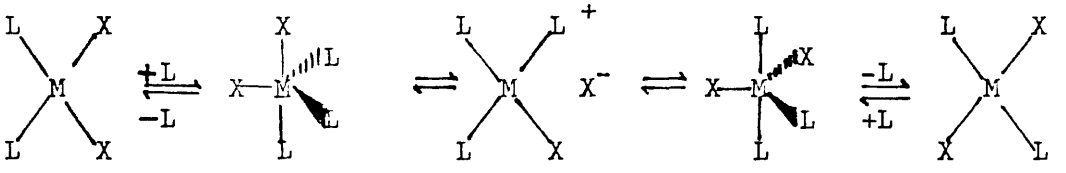
Cis-effects and cis-influences in square planar metal complexes are generally smaller than the analogous trans-effects or influences and they have consequently received less attention. Theoretical calculations[73] suggest that the cis influence of a ligand may only be slightly smaller than its trans-influence but recent[74] work is not in agreement. These investigations highlight the more significant contribution of steric effects to the magnitude of a cis-influence when measured from structural parameters. However, for the complexes cis$[PtCl_2(L)PEt_3)]$ L = Cl^-, $(H_2CPhN)_2C^-$, CNPh, $PhNH(OEt)C^-$, PEt_3 CO, $P(OPh)_3$ and PF_3 no correlations between bond-lengthening and bulk or between cis and trans influences were obtained.[75]

Qualitative determinations of cis and trans influences from techniques other than X-ray crystallographic analysis, such as NMR[71,72,74,75,76] infrared[77] or Mossbaur[78] spectroscopies, or from purely theoretical appraisals,[72,73] whilst in many specific instances providing good correlations with the structural data, are not always in agreement.

The interpretation of these discrepancies and an evaluation of the relative importance of δ - and π- contributions on a more general basis give the study of cis- and trans- influences a broad appeal.

Isomerisation of Square Planar Complexes

The consecutive displacement mechanism[65] is the best authenticated mechanism for the ligand catalysed isomerisation of a d^8 square planar complex. (Scheme II)



Scheme II A L = neutral ligand B X = halide

As nucleophilic displacements at platinum II are stereospecific it is obvious that two steps are necessary to facilitate isomerisation. The first step involves attack by the neutral ligand to form $[PtXL_3]^+X^-$ and the second is attack of halide on $[PtXL_3]^+$. If transition state A is formed in this step the reaction reverses, but should B result, isomerisation will occur. A pseudorotation mechanism converting A directly to B with no appreciable concentration of $[PtXL_3]^+X^-$ has been invoked to explain those reactions for which no ionic species was detected, or in those cases where difficulty was experienced when applying the consecutive displacement mechanism.[81] The different interpretations applied to the same ^{1}Hnmr spectroscopic data and the alternative explanations of the inhibiting role of added polar solvent on rates of isomerisation of $[PtI_2(PMe_2Ph)_2]$ by PMe_2Ph[82,83] highlight the inability of kinetic studies alone to decide between these two mechanisms. Roulet et al report more convincing evidence

for a consecutive displacement mechanism,[84] and a recent survey of isomerisation mechanisms views these different pathways as two extremes of a single process.[85]

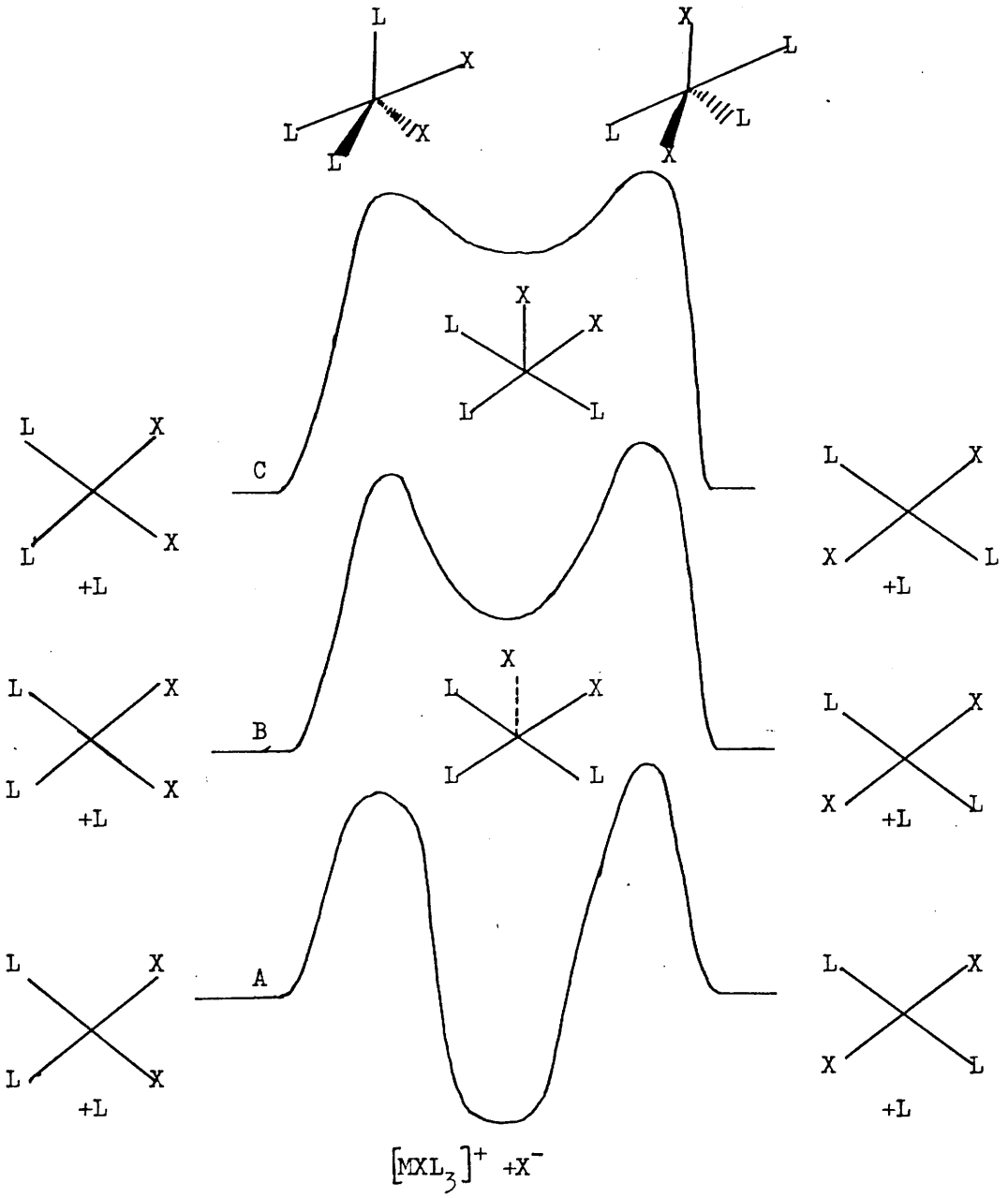
The three reaction profiles of Fig.I illustrate the effect of solvent polarity on the various pathways available in an isomerisation process. This explanation has been suggested on the basis of the reaction of trans-$[PtIPh(PR_3)_2]$ and CO in mixtures of C_6D_6 and $C_2H_2Cl_4$.[51]

Isomerisation by thermal, photochemical and dissociative means have been reported[85] and considerable debate has centred around the nature of the intermediates. Whilst Romeo and coworkers favour a dissociative process and a 14-electron 'T'-shaped intermediate for the isomerisation of cis-$[PtClR(PEt_3)_2]$ in MeOH[86] solution, Kelm et al[87] propose a pre-equilibrium solvolysis step and rapid displacement of solvent by X^- after the rate determining cis to trans isomerisation of the solvento intermediate. The study of isomerisation processes and the problems associated with data interpretation allied to the obvious flexibility of mechanistic arguments will continue to encourage research in this rewarding field of study.

Oxidative Addition

In the course of an oxidative addition reaction a metal complex adds an element-element bond of a covalent molecule to give a new complex in which both the coordination and oxidation numbers of the metal have increased by two:

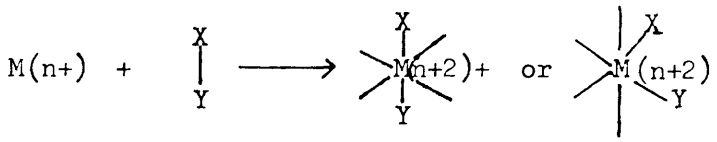
Figure I



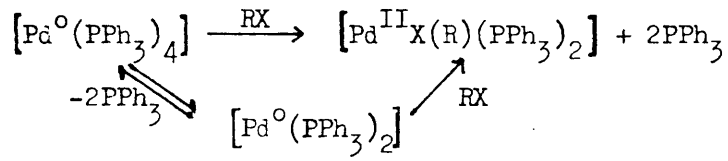
A: apolar solvent, e.g. benzene.

B: intermediate case.

C: polar solvent, e.g. $C_2H_2Cl_4$

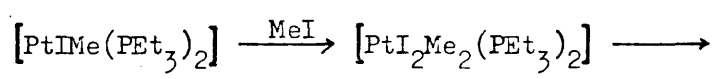


Zerovalent complexes undergo oxidative addition only after becoming coordinatively unsaturated by a dissociative process, particularly the zerovalent metal phosphine complexes.[32,88,89] (Equation 12)



(12)

In 1968 Vaska reported the reactions of trans-$[IrClCO(PPh_3)_2]$[90(i)] with simple covalent molecules (H_2, O_2, CO, Cl_2, CH_2CH_2, SO_2) and he discussed the effects of the metal, the covalent molecule, and the phosphine in this and other papers.[90(ii)(iii)] Chatt and Shaw[8] investigated the complexes $[PtX_2R_2(PEt_3)_2]$ made by the oxidative addition of halogens (X_2) or alkyl halides (RX) to suitable PtII complexes, and the subsequent reductive eliminations which produced different PtII complexes. (Equation 13)



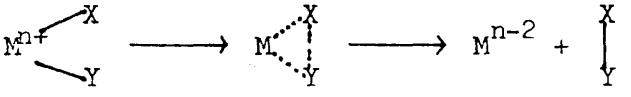
(13)

Other examples of the oxidative addition of hydrogen halides,[91] hydrogen cyanide,[91] olefins[90] and trialkyl germanium, tin and lead chlorides[92] are known.

In the literature the problem of cis or trans addition is still unresolved with evidence available to support either result. The mechanism of oxidative addition is thought to involve three possible pathways: an S_N2 process in which the metal acts as a nucleophile,[93] a concerted three centre addition[94] or a free radical process.[95]

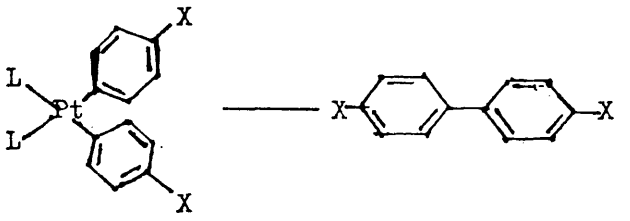
Reductive Elimination

The most evident feature of oxidative additions on unsaturated metal complexes is their reversibility. Reductive elimination is essentially the reverse of oxidative addition and it involves the concerted formation of a new bond between two previously ligated species. These species are lost, to leave the metal with lower oxidation and coordination numbers:



It has been suggested[96] that cleavage of metal-carbon σ-bonds generally proceeds, where possible, via an oxidative addition/reductive elimination pathway or alternatively by a normal S_E2 mechanism where this route is not available (i.e. for organo AuIII complexes). This explains the observation[96] that HCl reacts with cis-$[PtCH_3(p\text{-tolyl})(PMe_2Ph)_2]$ by cleaving the alkyl-metal bond via the former route, cis $[AuMe_2(p\text{-tolyl})(PPh_3)]$ reacts to give the dimethyl product $[AuMe_2Cl(PPh_3)]$ by electrophilic substitution. It has been reported[97] that reductive elimination involving cleavage of metal alkyl bonds is more facile than that involving metal-aryl bond cleavage.

The elimination of biphenyls from cis-diaryl complexes of PtII is an important example of the reductive elimination reaction and the kinetics and mechanism have been discussed.[98] A recent investigation[99] of para-disubstituted biphenyl elimination has proved beyond all doubt that the new carbon-carbon bond is formed exclusively between the carbon centres originally bound to platinum (equation 14).



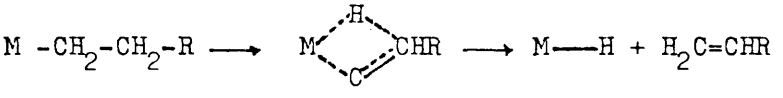
(14)

$L = PPh_3$, $X = OMe$, NMe_2, H

The effect of the substituents was to increase the temperature at which elimination occurred in the order - NMe_2> - OMe> -H.[99]

β-Elimination

Metal-alkyl complexes with secondary carbon centres in a β site to the metal and which are able to provide a vacant coordination site in the intermediate stages can decompose by β-elimination to give a metal-hydride and an olefin.[100] The olefin may enter the metal's coordination sphere. It is believed to be a concerted process involving a four-coordinate intermediate:



Pyrolysis of trans-$[PtClEt(PEt_3)_2]$ has been shown to cause elimination of ethylene with the formation of trans $[PtClH(PEt_3)_2]$.[8] The reaction is reversed with heat and high pressures of the olefin.[9]

To circumvent the possibility of β- elimination competing with and complicating the study of other reaction modes, it is advisable to use complexes with organic groups such as methyl or benzyl or block the coordination sites around the metal to prevent the hydrogen associating with the metal. Bulky phosphines, olefins and acetylacetonate are ligands which fulfil this latter role.[24]

α-Elimination

This is a much less well recognised process than β-elimination. It involves abstraction of hydride from an α-carbon to give a new metal-hydrido bond and an alkylidene moeity:

$$R'MCH_2R \rightleftharpoons R'\overset{H}{\underset{|}{M}}{=}CHR \rightleftharpoons R'H + M{=}CHR$$

The reaction of $[Ta\{CH_2C(CH_3)_3\}_3Cl_2]$ with two equivalents of neopentyl-lithium yields neopentane and an orange crystalline product, identified as a metal carbene complex (equation 15). The latter is formed by α-hydride abstration followed by α elimination of neopentane.[101]

$$[Ta\{CH_2C(CH_3)_3\}_3Cl_2] \xrightarrow[-2LiCl]{2(CH_3)_3(HLi} [Ta\{CH_2C(CH_3)_3\}_5] \longrightarrow \{(CH_3)_3(CH_2)\}Ta{=}C\begin{matrix}H\\ \diagdown\\ C(CH_3)_3\end{matrix} + C(CH_3)_4 \qquad (15)$$

Carbenes formed by α-hydrogen abstraction are thought to participate in the RhI catalysed dismutation of olefins[102] (equation 16). This particular reaction type is less common in the case of organo-platimum complexes.

$$\begin{matrix}Rh{=}CR_2^1\\ \uparrow\\ R_2C{=}CR_2\end{matrix} \rightleftharpoons \begin{matrix}CR_2^1\\ \diagdown\\ Rh \leftarrow \| \\ \|\\ CR_2\end{matrix} \qquad (16)$$

Internal Metallation

This reaction type is essentially the oxidative addition of a metal across an element-element bond of one of its own ligands, usually an addition across a carbon-hydrogen bond. Unless the complex thus formed is stable, given the reaction conditions prevailing at that

time, a reductive elimination step ensues which may be the reverse of the addition[103] or more likely be different. Internal metallations of purely aliphatic phosphines are known, notably where the alkyl side chains are bulky[104] but perhaps the most widely documented example is that of metallation across the ortho carbon-hydrogen bonds of coordinated aryl phosphines.[105] $[IrCl(PPh_3)_3]$[106] forms a stable hydrido-IrIII internally metallated complex when refluxed in benzene (equation 17) and $RhMe(PPh_3)_3$[107] loses methane giving a stable RhI complex upon similar treatment.

$$[Ir^{I}Cl(PPh_3)_3] \xrightarrow[\text{various solvents}]{\Delta} [Ir^{III}Cl(H)\{C_6H_4P(PPh_3)_2\}(PPh_3)_2] \quad (17)$$

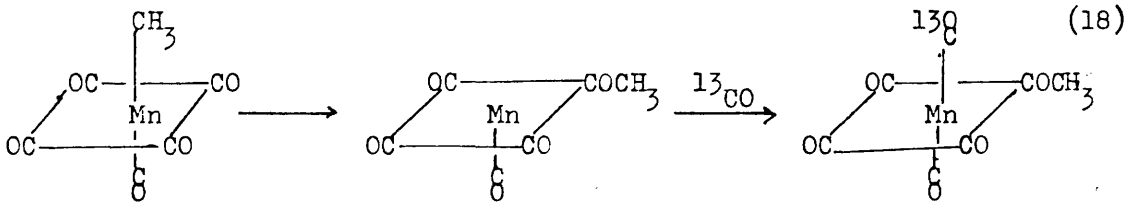
The Insertion Reaction

The insertion reaction may be represented in general terms as the addition of a metal compound M-X to an unsaturated molecule Y which has at least a lone pair of electrons available for reaction (or its equivalent):

$$M - X + :Y \longrightarrow M - Y - X$$

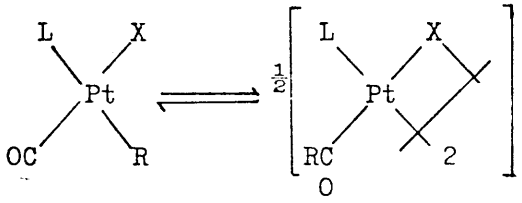
A very wide range of unsaturated molecules undergo insertion: olefins,[107] acetylenes,[108] CS_2,[109] CO,[110] isonitriles,[111] SO_2,[112] and others.[113]

The mechanism of carbonyl insertion has been established largely from investigations of the pentacarbonylmethyl manganese systems.[114] Labelled CO studies[115] have shown that the organic moeity participates in a [1,2] shift from the metal to the carbon of a coordinated CO in a *cis* position, and incoming CO resides in the vacated site (equation 18).



(18)

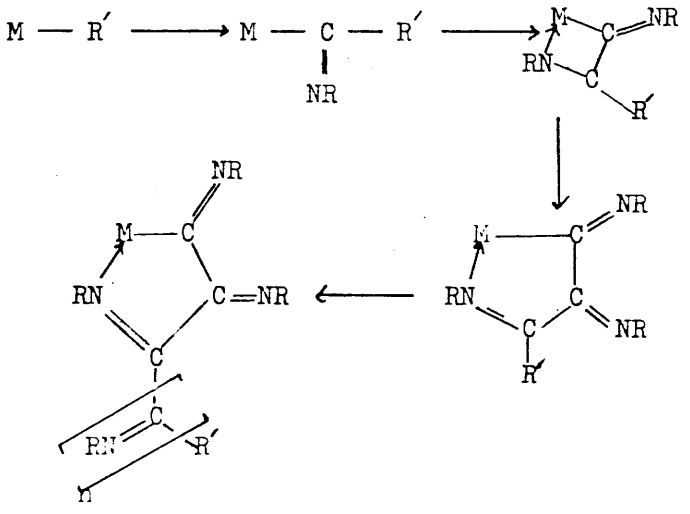
An entirely similar mechanism operates when $[CoIMe(CO)_4]$ reacts with PPh_3.[116] The reaction is more correctly referred to as an alkyl migration and not a 'carbonyl insertion'. However, the latter term suitably describes the product and today it is in common usage in the literature. Acyl-platinum and palladium complexes were first prepared[110] by Booth and Chatt from uncoordinated CO and the organo-metal complex. More recently insertion at PtII in the complexes $[PtXR(CO)L]$ (equation 19), has been investigated and the effects



(19)

of the neutral ligand L (tertiary phosphine or arsine), the halide X, and the organic group R have been qualitatively assessed.[116]

Isonitrile insertion reactions differ from those of carbon monoxide in several important and basic ways. Multiple insertion to give complexes of the type shown in Scheme III are known for NiII[117] and PdII.[118]



The stability of these complexes in the instances of double, triple and higher insertions is dependant upon nitrogen lone pair donation to the metal to form a four- and then a five- membered ring.[118] The polymeric chain of inserted isonitriles are also stable. These successive insertion reactions were proposed as a mechanism for the catalytic polymerisation of isocyanides by transition metal complexes. Double carbonyl insertions, let alone multiple insertions, are extremely rare despite theoretical and practical interest. However, aryl-pyruvic acid salts have been reported[119] from the reaction of $[Co_2(CO)_8]$ with substituted benzyl chlorides under phase transfer catalytic conditions.

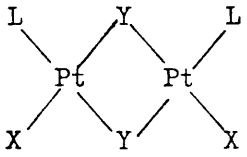
Where there is a choice within one molecule the isonitrile insertion wins out over migration of alkyl to carbon monoxide.[120] Theoretical calculations[121] of both processes show that the former process has an activation barrier ca. 1 e.V. higher than the latter for insertion in octahedral complexes of Mn, and the authors add that the reaction is highly sensitive to acid catalysis. Steric effects are important in the isocyanide insertion reaction with the bulkier isonitriles such as tert-BuNC being less favourable towards insertion than say CyNC[120] in analogous complexes. Finally, an important advantage to the use of isocyanides as ligands is the way we can vary the organic substituent on the nitrogen, and thus vary their properties, in a similar manner to the way phosphine ligands can be altered.

CHAPTER TWO

ASYMMETRICAL CLEAVAGE OF HALIDE-BRIDGED PLATINUM DIMERS

Chapter 2 - Introduction

Towards the end of the transition series many binuclear ligand-bridge complexes of the d^8 ions are known, and they are particularly numerous for square planar coordinated PdII and PtII. For the platinum derivatives the strength of the bridge-bonds has been found to decrease in the series I>Br>Cl[122,123] and R_2P>RS>Et_2PO>Cl.[124] Monodentate ligands can break the weaker bridges (equation 1) (usually all but RS, R_2P[124,125] and OH[125,126] for PtII) making a useful and widely applied synthetic route.



$$+2L' \longrightarrow 2[PtXYLL'] \qquad (1)$$

Kinetic studies[122,127] on the bridge cleavage reactions of PtII complexes revealed rate law(2), which is similar to those obtained

$$\text{rate} = (k_1 + k_2[L'])\,[\text{dimer}] \qquad (2)$$

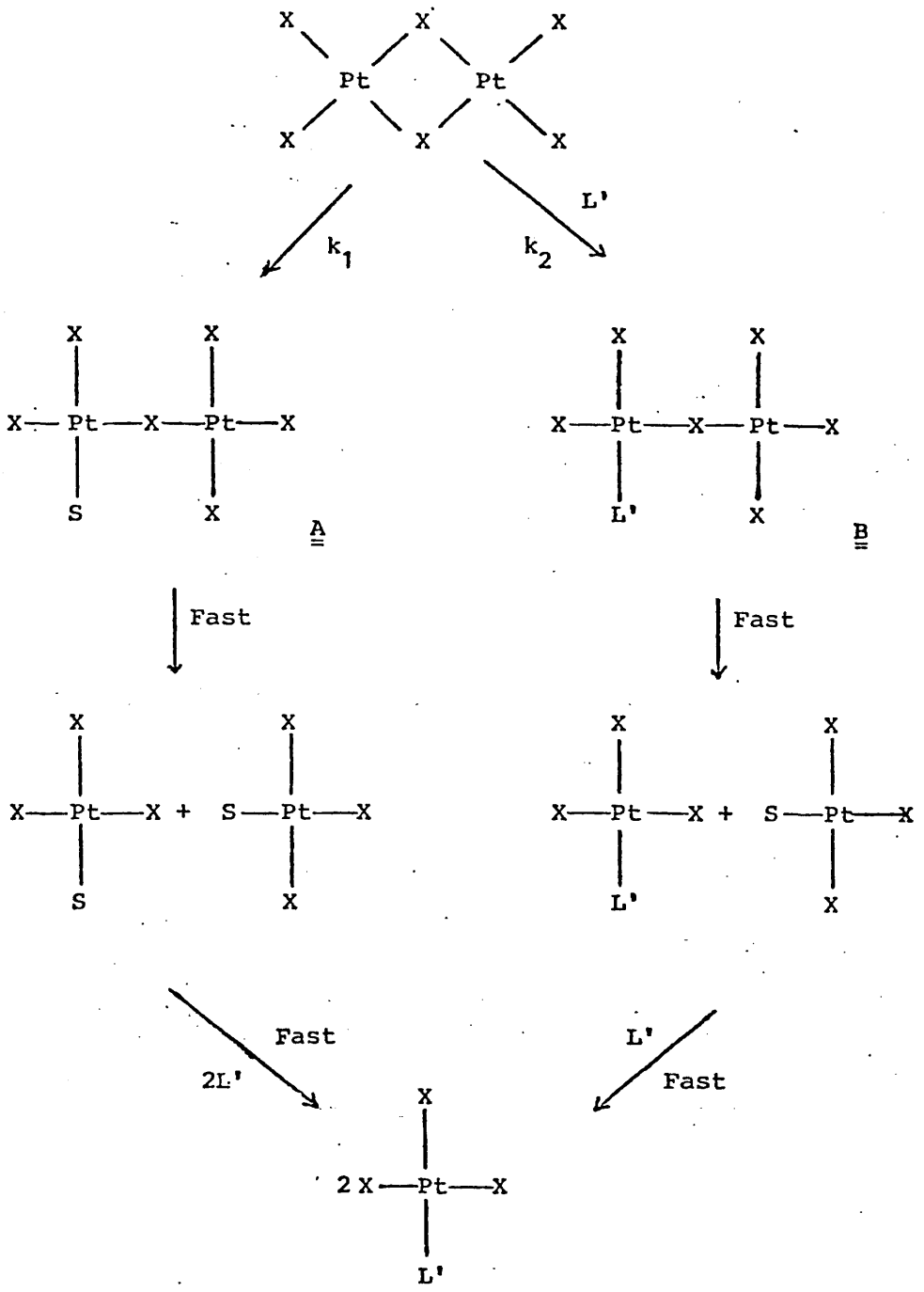
for ligand substitutions of square-planar monomeric complexes. This rate expression is compatible with the two reaction pathways of Scheme 1 (S = solvent), operating simultaneously. The rate law associated with bidentate entering ligands is the same[127] but the products are not symmetrical (3). This result implied that

$$[Pt_2X_6]^{2-} + L\text{—}L \longrightarrow \underline{cis}[PtX_2(L\text{—}L)] + [PtX_4]^{2-} \qquad (3)$$

singly-bridged intermediates like A and B of Scheme I were sufficiently long lived to persist until chelation with the bidentate ligand. Single-bridged binuclear species have been postulated as intermediates in other reaction systems.[128]

Two isomers can be produced when $[Pt_2(\mu\text{-}X)_2Y_2L_2]$ or $[Pt_2(\mu\text{-}X)_2X_2L_2]$ (where L are neutral ligands) are cleaved by monodentate ligands.

SCHEME 1



SCHEME 1

The bond opposite the terminal ligand of higher trans-effect[122] is generally found to be that which is broken. Equations (4) and (5) illustrate this clearly, where the order of trans-effect is olefin>Cl>am (= amine).[34] It is often the case that the

$$[Pt_2Cl_4(am)_2] + 2C_2H_4 \longrightarrow 2\ \underline{cis}\ [PtCl_2(am)(C_2H_4)] \quad (4)$$

$$[Pt_2Cl_4(C_2H_4)_2] + 2\ am \longrightarrow 2\ \underline{trans}\ [PtCl_2(am)(C_2H_4)] \quad (5)$$

initial (kinetic) product isomerises to the thermodynamically stable form.[34,129] Traces of free ligand readily catalyse these isomerisations.[85] Therefore great care may be necessary to produce the kinetic isomer, and deduce the reaction course from the products detected. In spite of these findings, isomer ratios have been interpreted as an indication of the relative trans effects of X^- and L (equation 1).[130] However, little attention has been paid to the isomeric nature of the products in the majority of applications of this reaction.

When the geometry of the reaction products is considered, the first indications are obtained that bridge cleavage reactions may not be as well ordered as implied above. Bridge cleavage by CO of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ in $CDCl_3$ at -60°C produces almost exclusively the isomer with CO trans to $PMePh_2$[51] and yet the aryl dimer itself exists in solutions as both cis and trans isomers. Although cis and trans forms of these halide-bridged dimers equilibrate rapidly,[51,131] the singularity of the product is not easy to explain. Pearson and Muir have suggested that the opening of the second bridge (probably by solvent) may not be independent of the first cleavage.[122]

The appearance in some cases of non-symmetrical products is a second area of concern. Where bidentate ligands have been added their production is common and unremarkable (equation 3)[127,132] but in the reactions of monodentate ligands such products can be difficult to account for[133] (equations 6 and 7).

$$[Pt_2X_4]^{2-} + 2L \longrightarrow [PtX_2L_2] + [PtX_4]^{2-} \quad (6)$$

$$[Pt_2X_4L_2] + 2L' \longrightarrow [PtX_2L_2] + [PtX_2L'_2] \quad (7)$$

A disproportionation of the initial products[34,129,134] provides one possible explanation (equation 8). Processes such as these

$$2[PtX_2LL'] \longrightarrow [PtX_2L_2] + [PtX_2L'_2] \quad (8)$$

are well documented, and the natures of the metal, ligands and solvents influence the equilibria.[122,135] These processes, too, are catalysed by traces of free ligand,[82] though spontaneous examples abound (they may in fact be solvent catalysed or auto-catalysed, like isomerisations)[85] especially among palladium compounds. Without detailed mechanistic investigations the possibility of ligand transfer between metal atoms during cleavage cannot be discounted. This possibility has been proposed[136] for some nickel complexes, though a disproportionation pathway could be operating.

Finally, a few bridge-cleavage reactions have been reported to proceed, then later to reverse, eliminating the cleaving ligand.[137] These reactions were slow and temperature dependent.

Results and Discussion

The reactions of tri-n-butylphosphine and $[Pt_2Cl_4(Bu^n{}_3P)_2]$ or $[Pt_2Cl_4(PMe_2Ph)_2]$ respectively and of dimethylphenylphosphine with

$[Pt_2Cl_4(PMe_2Ph)_2]$ or $[Pt_2Cl_4(PBu^n_3)_2]$ respectively were examined in detail by $^{31}P-\{^1H\}$ nmr. spectrometry. The product distribution was critically dependent on both the reactants and the conditions.

The addition of one equivalent of Bu^n_3P to $[Pt_2Cl_4(PBu^n_3)_2]$ in deuteriochloroform was the simplest reaction. Only trans-$[PtCl_2(PBu_3)_2]$ and unreacted $[Pt_2Cl_4(PBu_3)_2]$ remained after reaction at either -60°C or ambient temperature. Clearly a normal bridge cleavage reaction operates (equation 9) and conforms to Scheme I and equations (1) and (5).

$$\text{trans-}[Pt_2Cl_4(PBu_3)_2] + 2\ PBu_3 \longrightarrow 2\ \text{trans-}[PtCl_2(PBu_3)_2] \qquad (9)$$

A more complicated reaction occurred upon the addition of 1 equivalent of PMe_2Ph to one of trans-$[Pt_2Cl_4(PMe_2Ph)_2]$ in $CDCl_3$. The stoichiometry of the reaction was the expected two equivalents of phosphine to one of dimer (in all cases, ^{31}P nmr spectra revealed that 50% of the dimer remained unreacted). Only 10-15% of the reaction products was $[PtCl_2(PMe_2Ph)_2]$ at -60°C, with both trans and cis isomers present and the trans form predominating. The remainder consisted of the ions $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PMe_2Ph)]^-$ in a 1:1 ratio. By preparing them independently according to published procedures, they were identified unambiguously (equations 10 and 11).

$$\text{cis}[PtCl_2(PMe_2Ph)_2] + PMe_2Ph \longrightarrow [PtCl(PMe_2Ph)_3]Cl \qquad (10)$$

$$[Pt_2Cl_4(PMe_2Ph)_2] + 2\ Et_4N\ Cl \longrightarrow 2[Et_4N][PtCl_3(PMe_2Ph)] \qquad (11)$$

The products from this dimer cleavage reaction were unchanged in solution at -60°C for several hours, but when the mixture was allowed to come to room temperature the ionic materials disappeared and the final products were cis- and trans- $[PtCl_2(PMe_2Ph)_2]$ (1:1,

equation 12) still with unreacted $[Pt_2Cl_4(PMe_2Ph)_2]$. This transformation from ionic to neutral materials probably proceeds via phosphine attack on the anion and halide attack on the cation. The interaction of Cl^- with $[PtCl(PMe_2Ph)_3]^+$ leads exclusively to cis-$[PtCl_2(PMe_2Ph)_2]$ (see below), and from trans-effect considerations it is not unreasonable to presume that PMe_2Ph produces trans-$[PtCl_2(PMe_2Ph)_2]$ from $[PtCl_3(PMe_2Ph)]^-$.

$$[PtCl(PMe_2Ph)_3]^+ + [PtCl_3(PMe_2Ph)]^- \longrightarrow \underline{trans}[PtCl_2(PMe_2Ph)_2] + \underline{cis}\ [PtCl_2(PMe_2Ph)_2] \qquad (12)$$

At room temperature the reaction between $[Pt_2Cl_4(PMe_2Ph)_2]$ and PMe_2Ph produced only cis and trans $[PtCl_2(PMe_2Ph)_2]$.

The additions of PBu^n_3 to $[Pt_2Cl_4(PMe_2Ph)_2]$ and of PMe_2Ph to $[Pt_2Cl_4(PBu_3)_2]$ were the most complicated reactions. In three experiements 0.5, 1.0 and 1.9 molar equivalents of PMe_2Ph were added by syringe to deuteriochloroform solutions of $[Pt_2Cl_4(PBu_3)_2]$ at -60°C and $^{31}P-\{^1H\}$ nmr. spectra of the mixtures were recorded at this temperature. As well as signals from the expected trans-$[PtCl_2(PBu_3)(PMe_2Ph)]$ which was the major product, and resonances from unreacted dimer, cis-$[PtCl_2(PBu^n_3)(PMe_2Ph)]$ (cis:trans ratio 2:3) trans$[PtCl_2(PBu_3)_2]$, $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl_3(PBu_3)]^-$ were identified. Along with several unidentified minor products which had nmr signals grouped in doublets (J ca 20Hz) was a trace of trans-$[PtCl(PBu_3)_2(PMe_2Ph)]^+$. These unidentified doublets probably correspond to other mixed phosphine cations. The anion: cation ratio when measured was close to 1:1 and the relative amounts of ionic material increased with increasing added phosphine to a maximum of about 35% when 1.9 equivalents of PMe_2Ph were used. The amount of trans-$[PtCl_2(PBu_3)_2]$ also increased with increasing PMe_2Ph.

During several hours at -60°C no changes were observed in these spectra, but when the solutions were warmed to room temperature signals from the ionic species disappeared and resonances from cis-$[PtCl_2(PMe_2Ph)_2]$ grew in strength. The cis-trans ratio of the mixed phosphine product $[PtCl_2(PBu_3)(PMe_2Ph)]$ did not alter, whilst the final ratio of cis$[PtCl_2(PMe_2Ph)_2]$ to trans-$[PtCl_2(PBu_3)_2]$ was about 1:1. These same final products were obtained when $[Pt_2Cl_4(PBu_3)_2]$ reacted with one equivalent of PMe_2Ph at ambient temperature.

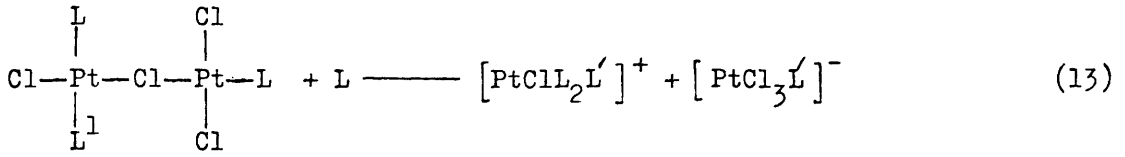
Similar results were produced when 0.6, 1.0 and 2.0 equivalents of PBu_3 were allowed to react with $[Pt_2Cl_4(PMe_2Ph)_2]$ in $CDCl_3$ at -60°C, but the minor products differed. Trans-$[PtCl_2(PBu_3)(PMe_2Ph)]$ was again the major product, and unreacted dimer was present except where two equivalents of phosphine had been added. No cis-$[PtCl_2(Bu_3P)(PMe_2Ph)]$ or trans-$[PtCl_2(PBu_3)_2]$ were evident but a wider variety of ionic species were present, with $[PtCl_3(PMe_2Ph)]^-$ and trans-$[PtCl(PMe_2Ph)(PBu_3)_2]^+$ predominating and $[PtCl(PMe_2Ph)_3]^+$ and $[PtCl(PBu_3)_3]^+$ identified amongst the remainder. As in previous reactions, the importance of the ionic materials grew with increasing added phosphine, rising to ca 35% for two equivalents. Again, although many of the signals assigned to minor cationic species could not be identified, coupling constants typical of Jpp in cis-diphosphine platinum complexes (ca 20Hz) were apparent. The overall intensities calculated for the ^{31}P signals assigned to the cations were three times that of the signals from $[PtCl_3(PMe_2Ph)]^-$.

During several hours at -60°C spectra of these mixtures did not

change, but as before when the solutions warmed to room temperature the salts disappeared and $[PtCl_2(PBu_3)_2]$ (cis :trans ,10:1) and cis-$[PtCl_2(PMe_2Ph)_2]$ became apparent instead. In all three reactions isomerisation of the mixed phosphine product did proceed at room temperature, resulting eventually in total conversion to cis-$[PtCl_2(PBu_3)(PMe_2Ph)]$. Similar final products were obtained from the room temperature reaction of PBu_3 and $[Pt_2Cl_4(PMe_2Ph)]$ but no cis-$[PtCl_2(PBu_3)_2]$ or cis-$[PtCl_2(PMe_2Ph)_2]$ was apparent.

The ionic species are the most surprising products obtained from the low temperature reactions and two distinct routes could produce such materials. Firstly, the principal bridge cleavage products (trans-$[PtCl_2(PMe_2Ph)_2]$ or trans-$[PtCl_2(PBu_3)(PMe_2PH)]$) by reacting with the added phosphine could produce cations by Cl^- elimination, which in turn could cleave the unreacted dimer to produce the observed anions in processes analogous to (10) and (11). It has been confirmed by independent experiments that when PMe_2Ph or PBu_3 is added to trans-$[PtCl_2(PBu_3)(PMe_2Ph)]$, or when PBu_3 is added to cis-$[PtCl_2(PMe_2Ph)_2]$, the cationic products formed include those observed from the mixed phosphine dimer cleavages.

The second plausible route to these ionic species involves attack of the necessary second incoming nucleophile at the same platimum atom of the dimer as the first one. This reaction would occur at the singly bridged intermediate corresponding to B of Scheme I (13) to produce an anion-cation pair. If solvent attack had resulted in bridge-opening, rather than phosphine, there seems no reason why this should not behave similarly.



(13)

Such singly bridged intermediates are known to have appreciable lifetimes.[127,128]

The cations are not random in their arrangement of phosphine ligands: $[PtCl(PMe_2Ph)_3]^+$, $[PtCl(PBu_3)_3]^+$ and <u>trans</u>-$[PtCl(PBu_3)_2(PMe_2Ph)]^+$ figure prominently in the addition reactions of both phosphines. A process of phosphine exchange leading to products which are thermodynamic and not kinetic in origin could account for this. Rapid room temperature exchange of phosphines between $[PtCl(PMe_2Ph)_3]^+$ and <u>cis</u>$[PtCl_2(PMe_2Ph)_2]$ has been reported from ^{1}Hnmr studies[82] and this has been confirmed by ^{31}Pn.m.r. spectrometry. When 0.6 mole equivalents of Ph_2MeP were added to <u>cis</u>$[PtCl_2(PMe_2Ph)_2]$ in $CDCl_3$, signals from both the cation and the <u>cis</u> complex were distinct at -60°C, whilst at +30°C the signals broadened considerably, indicative of rapid ligand exchange. Similar processes operating in our bridge cleavage reaction would seem to indicate the secondary attack mechanism (equations 10 and 11) as the route to the ionic products.

However, two facts are not in accord with this explanation. Firstly, the rate of bridge cleavage is reported to be 10^3 times faster than ligand substitutions at square planar platinum.[122] Upon examining the reaction of PMe_2Ph and $[Pt_2Cl_4(PMe_2Ph)_2]$ in $CHCl_3$ by stopped-flow kinetic methods, the pseudo-first order rate constant was determined as 4.3 $l.mol.^{-1}s^{-1}$ at 20°C. Although the reaction of tertiary phosphine with monomeric platinum was

too slow to follow by these methods, published data[82] give a rate constant of 1.3×10^{-3} $l.mol.^{-1}s^{-1}$ for phosphine exchange at cis-$[PtI_2(PMe_2Ph)_2]$ at 38°C in methanol. These data confirm the generality of Pearson's observations. Secondly, in most of the reactions studied excess halide-bridge dimer was present and any phosphine released from the cations by halide attack[82] would be rapidly consumed by the dimer. At -60°C the ionic materials survived unchanged in the presence of the dimers, therefore is it concluded that no phosphines were released from the final products (and hence no ligand exchange takes place) at this temperature.

Another possibility remains to be examined: that a secondary reaction of phosphine with the primary cleavage products could occur prior to complete mixing of the reactants, in those regions of the reaction mixture where locally high concentrations of added phosphine were temporarily present (equation 10). The dimer could then be cleaved by halide released from such a reaction to give the observed anion. Using a tangentially arranged two jet glass mixing apparatus and capillary to achieve fast mixing of equimolar dimer and phosphine solutions, the experiments which produce ionic materials were repeated several times. The whole assembly was maintained at either -60°C ($CDCl_3$ solutions) or -78°C (with $CDCl_3/CH_2Cl_2$ solvent mixture) and the mixtures were delivered directly into 5mm O.D. N.M.R. tubes.

The proportion of ionic material produced from the reaction between $[Pt_2Cl_4(PMe_2Ph)_2]$ and PMe_2Ph at low temperature was invariant with the method of mixing. The ionic species $[PtCl_3(PMe_2Ph)]^-$ and

$[PtCl(PMe_2Ph)_3]^+$ accounted for 85% of the products after mixing pure liquid PMe_2Ph with solutions of the dimer, adding PMe_2Ph as a solution, or by rapid tangential mixing. This is taken as evidence that the mechanism operating in this case is asymmetrical attack of two phosphine ligands at one platinum centre of the dimer (equation 13 Scheme 2).

When tangential mixing of solutions was employed for the reactions of $(PBu_3)_2$ with $[Pt_2Cl_4(PMe_2Ph)_2]$ and for PMe_2Ph with $[Pt_2Cl_4(PBU_3)_2]$, the proportions of ionic products were markedly reduced to ca 5%. Under normal mixing conditions therefore most of the ionic compounds arise from secondary interactions in local phosphine-rich neighbourhoods, but in this case it is probable that they originate via mechanism 13. Inhomogeneous reaction conditions have resulted in unexpected products in other cases.[139]

It is clear that the nature of the products changes with the phosphines employed. In these reactions less ionic materials result where PBu_3 is involved (either as 'resident' or incoming nucleophile) than with PMe_2Ph. Indeed, when two mole equivalents of PBu_3 were added to $[Pt_2Cl_4(PBu_3)_2]$ no ionic materials were detected at all. $^{31}P\{^1H\}$nmr spectroscopic parameters for the complexes identified in these reactions are given in Table I.

Before it was recognised that some of the products of these bridge cleavage reactions resulted from local high concentrations of added nucleophile reacting with the primary bridge cleavage products, (especially in those reactions where phosphine as neat liquid was added to solutions of dimer), two other mechanistic pathways were

SCHEME 2

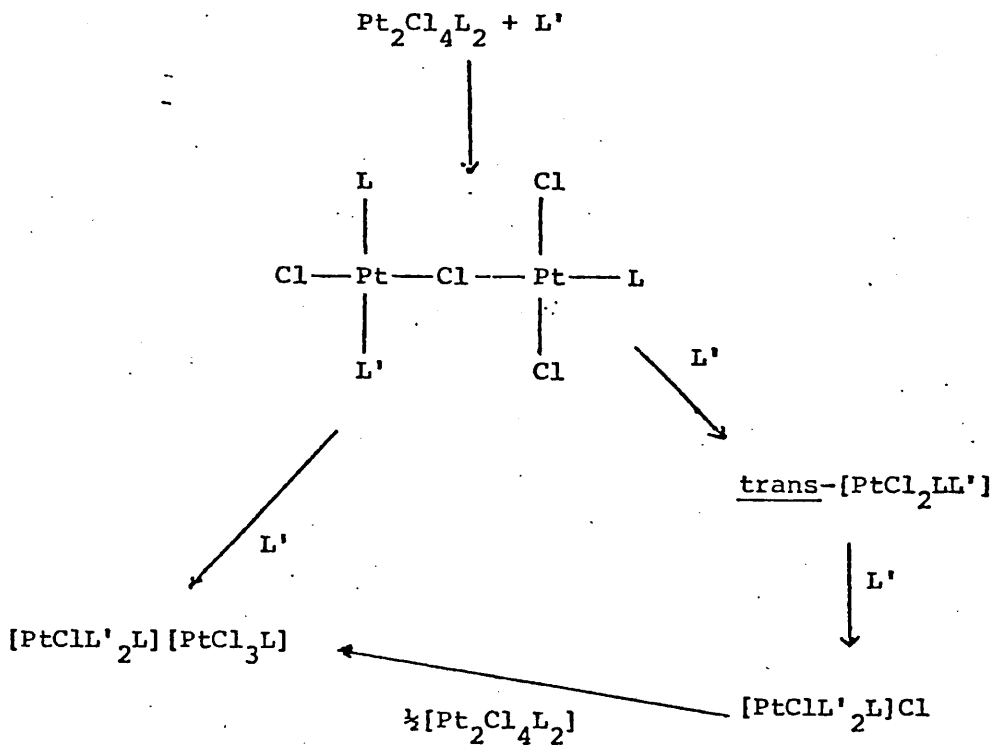

Pt2Cl4L2 + L'
L
Cl
Cl—Pt—Cl—Pt—L
L'
Cl
L'
trans-[PtCl2LL']
L'
L'
[PtClL'2L][PtCl3L]
[PtClL'2L]Cl
½[Pt2Cl4L2]

TABLE I

^{31}P n.m.r.[a] parameters of identified species from the reactions of PBu_3/PMe_2Ph with $[Pt_2Cl_4(PBu_3)_2]/[Pt_2Cl_4(PMe_2Ph)_2]$

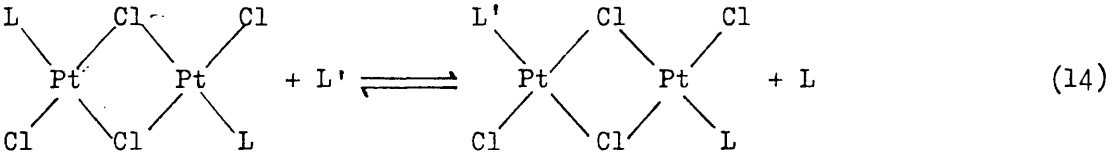
Complex	$\delta(P)$/ppm[b]	^1J(Pt-P)/Hz	^2J(P-P)/Hz	Reference
$[Pt_2Cl_4(PBu_3)_2]$	+4.0	3720		71
$[Pt_2Cl_4(PMe_2Ph)_2]$	-16.3	3861		this work
$[PtCl(PBu_3)_3]^+$[c]	+10.9d	2266	19.2	76
	-1.1t	3459	19.2	
$[PtCl(PMe_2Ph)_3]^+$	-3.4d	2302	21.4	this work
	-16.4t	3520	21.4	
$[PtCl_3(PBu_3)]^-$	-5.2	3790		142
$[PtCl_3(PMe_2Ph)]^-$	-20.6	3656		this work
trans-$[PtCl_2(PBu_3)_2]$	+4.3	2349		71
cis-$[PtCl_2(PBu_3)_2]$	+1.0	3521		71
trans-$[PtCl_2(PMe_2Ph)_2]$	-7.6	2407		141
cis-$[PtCl_2(PMe_2Ph)_2]$	-14.2	3540		141
trans-$[PtCl_2(PBu_3)(PMe_2Ph)]$	+4.8	2340	470	76
	-6.7	2330	470	
cis-$[PtCl_2(PBu_3)(PMe_2Ph)]$	+0.4d	3371	18.6	76
	-14.0d	3710	18.6	
trans-$[PtCl(PBu_3)_2(PMe_2Ph)]^+$	+8.5d	2206	21.1	76
	-11.2t	3507	21.1	

(a) In $CDCl_3$ at -60°C

(b) Relative to external H_3PO_4: positive is downfield d = doublet t = triplet.

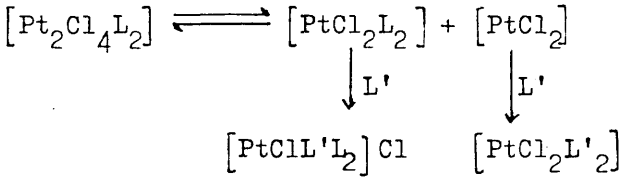
(c) Literature values, recorded at room temperature.

considered. Firstly, the possibility of exchange of incoming and 'resident' nucleophiles to give mixed dimeric platinum complexes. This could conceivably have occured via a reversible first step in the bridge cleavage reaction which eliminated the 'resident' phosphine and not the cleaving ligand (equation 14).



(14)

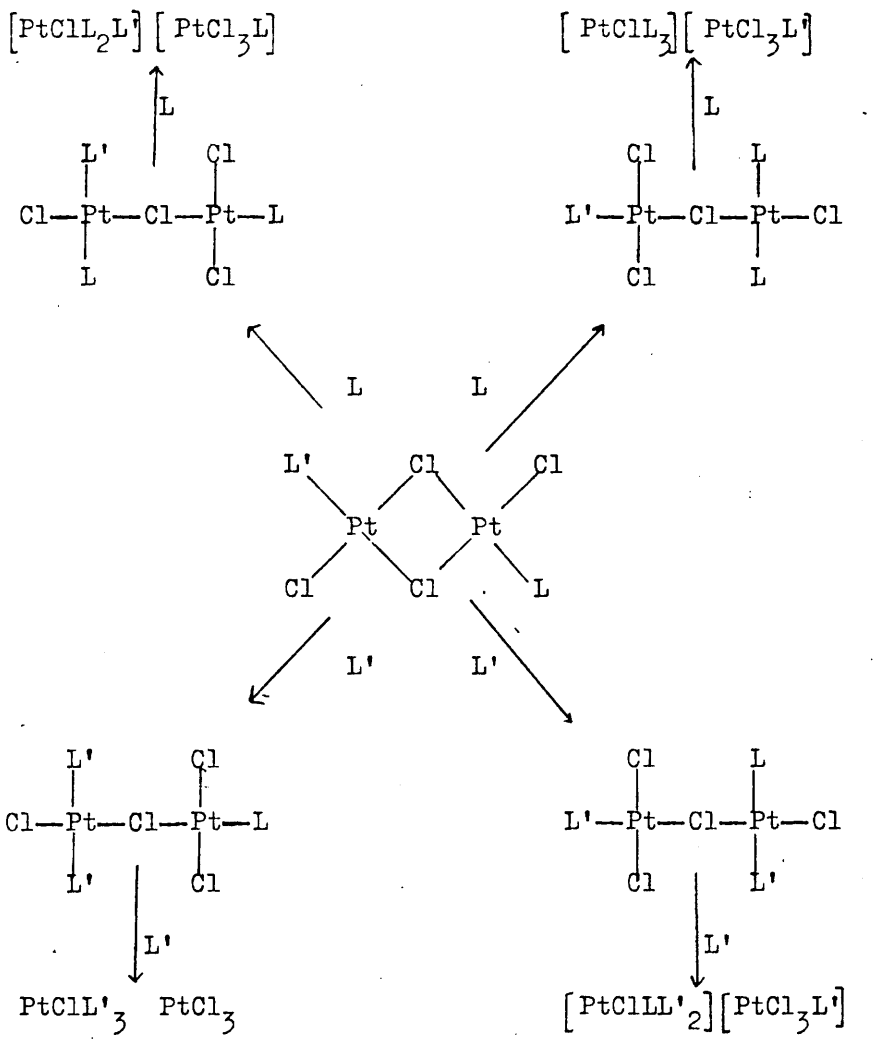
Secondly a disproportionation of the original dimer to $[PtCl_2L_2]$ and $[PtCl_2]$, which could then react with the incoming nucleophile giving salts and neutral monomers respectively (equation 15).



(15)

Scheme 3 illustrates how asymmetric cleavage of the mixed dimer by L or L' (L, L' as in 14) could give rise to ionic components, including the anionic species of both phosphines. However, only those anions with the same phosphine as the parent symmetric dimer are observed. $[Pt_2Cl_4(PBu_3)_2]$ and $[Pt_2Cl_4(PMe_2Ph)_2]$ react in $CDCl_3$ to give a new complex with two broad ^{31}P resonances (Table II): assigned to the mixed dimer $[Pt_2Cl_4(PBu_3)(PMe_2Ph)]$. These signals are not observed in the reactions of Bu_3P with $[Pt_2Cl_4(PMe_2Ph)_2]$ or of PMe_2Ph with $[Pt_2Cl_4(Bu_3P)_2]$. If exchange were prevalent and cleaving of the new dimer was as fast as it is for each of the symmetric complexes, detectable amounts should be left in excess when deficiencies of phosphine are added. The absence of the mixed dimer and the appearance of only one anion, is taken as evidence that the exchange process does not operate.

SCHEME 3


[PtClL2L'][PtCl3L]
[PtClL3][PtCl3L']
L
L'
Cl
Pt
L
L'
Cl
Pt
L
L
L
L'
L'
PtClL'3
PtCl3
[PtClLL'2][PtCl3L']

In the reactions of $[Pt_2Cl_4(PMePh_2)_2]$ with CNPh, and of Bu_3P with $[Pt_2Cl_4(PMePh_2)_2]$ the large concentrations of cis-$[PtCl_2(PMePh_2)_2]$ seemed to suggest that a disporportionation of dimer had occurred (equation 15). $[PtCl_2(CNPh)_2]$ is a likely component of the first reaction, and trans-$[PtCl_2(PBu_3)_2]$ is apparent in the second experiment in accord with a possible reaction of $[PtCl_2]$ and either ligand (equation 15). Phosphorus-31 n.m.r. studies of the dimer itself were complicated by its very poor solubility. However, slight heating did result in the production of small amounts of cis-$[PtCl_2(PMePh_2)_2]$, but no obvious precipitate was noted. Both $[Pt_2Cl_4(PMe_2Ph)_2]$ and $[Pt_2Cl_4(PBu_3)_2]$ were unaffected by heating in $CDCl_3$. Whether disporportionation has occurred for the $PMePh_2$ complex is unclear, but studies of a more soluble alternative e.g. $[Pt_2Cl_4\{P(p\text{-tolyl})_3\}_2]$, might clarify this possibility.

Lastly there exists the possibility that the reactant dimer was contaminated by small amounts of cis-$[PtCl_2(PMePh_2)_2]$ remaining from the preparative route (equation 16). As the preparative

$$\text{cis-}[PtCl_2)PMePh_2)_2] + [PtCl_2] \xrightarrow[24 \text{ hours}]{\text{reflux } C_2H_2Cl_4} [Pt_2Cl_4(PMePh_2)_2] \qquad (16)$$

route is clean and owing to its poor solubility, the dimer is used without purification. Small amounts of cis-$[PtCl_2(PMePh_2)_2]$ (ca 6%) are noted when a suspension of the dimer is treated with excess $[Et_4N]^+Cl^-$ (the main product being $Et_4N^+[PtCl_3(PMePh_2)]^-$). Although significant, this concentration of contaminant is far lower than the typical concentrations of $[PtCl_2(PMePh_2)_2]$ observed in the cleavage reactions (ca 40-45%).

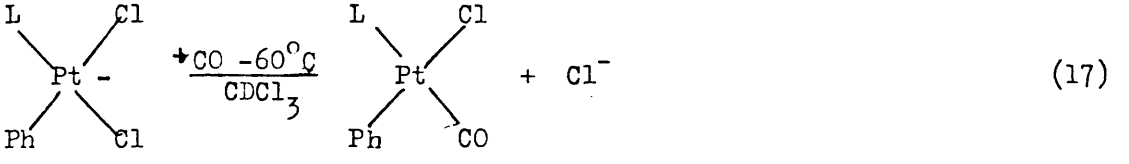
It has been reported[51] that sulphur, by oxidising free phosphine, was helpful in elucidating other mechanistic pathways in the carbon-

ylation of trans-$[PtXR(PR_3)_2]$. Two dimer cleavage reactions were performed in the presence of sulphur: (i) PBu_3 added as pure liquid to a suspension of $[Pt_2Cl_4(PMePh_2)_2]$ in $CDCl_3$, and (ii) $PMePh_2$ was added to a $CDCl_3$ solution of $[Pt_2Cl_4(PBu_3)_2]$. In neither case were the sulphides of the 'resident' phosphines noted. For (i) the products at -60°C were trans-$[PtCl_2(SPBu_3)(PMePh_2)]$ and cis-$[PtCl_2(PMePh_2)_2]$, the former isomerising to the cis- form upon warming to room temperature. In the second experiment cis-$[PtCl_2(PBu_3)(SPMePh_2)]$ was noted at +30°C and -60°C, whilst at the lower temperature $[PtCl(PBu_3)(PMePh_2)_2]^+$ and $[PtCl_3(PBu_3)]^-$ appeared along with trans-$[PtCl_2(PBu_3)_2]$, which was also prominent at room temperature.

Clearly from these results we can say that Bu_3P reacts more rapidly with sulphur than it does with $[Pt_2Cl_4(PMePh_2)_2]$ and that Bu_3PS cleaves the dimer in an orthodox fashion to give the expected trans product. Diphenylmethylphosphine on the other hand reacts with sulphur and $[Pt_2Cl_4(PBu_3)_2]$ at comparable rates: the sulphide cleaves the dimer in an orthodox fashion, but only cis$[PtCl_2(PBu_3)(SPMePh_2)]$ is stable, and the phosphine itself either had mixed inhomogeneously with the dimer (which was likely) or had cleaved the dimer asymmetrically.

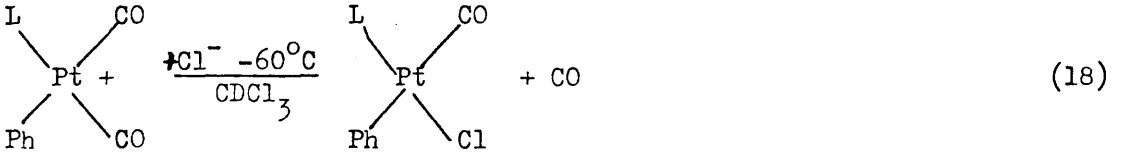
If the organo-platinum dimer $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ (which exists in solution as rapidly equilibrating cis and trans isomers) were cleaved asymmetrically by CO, components of the type $[PtCl_2Ph(PMePh_2)]^-$ and $[PtPh(CO)_2(PMePh_2)]^+$ might be produced which could rearrange at -60°C to give largely isomer III. Whilst cis-$[Et_4N][PtCl_2Ph(PMePh_2)]$ certainly reacts with CO at -60°C to give exclusively isomer III (equation 17) cis$[PtPh(CO)_2(PMePh_2)]SO_3CF_3$ was found to react with

$Et_4N^+Cl^-$ to give only isomer II (equation 18). Accordingly it is unlikely that asymmetric cleavage and subsequent rearrangement of ionic species such as these operates (at -60°C), and another explanation for the singularity of the cleavage products must be sought.



(17)

III



(18)

II

Whilst it is still possible that phosphine exchange and isomerisation reactions could take place at the singly-bridged intermediates, it is clear that no simple exchange between incoming and 'resident' nucleophiles occurs, because the anions observed are exclusively those with the same phosphine as the dimer. For this same reason neutral ligand exchange at the anions is also unlikely, as is the migration of phosphines from metal to metal suggested by Coronas et al.[136]

At no time was any evidence obtained for the presence in solution of singly bridged intermediates, even although most reactions were performed with excess dimer. It seems likely that even at -78°C such species rearrange or react further in the time to complete spectroscopic analysis (5-10 minutes).

TABLE II

Miscellaneous ^{31}Pn.m.r.[a] Parameters of Platinum II Complexes

	$\delta(P)$[b] p.p.m.	$^1J(P,Pt)$/Hz	$^2J(P,Pt)$/Hz	$^2J(P,P)$/Hz	$^3J(P,P)$/Hz
cis-$[PtCl_2(PBu_3)(PMePh_2)]$	-1.38	3763		16.5	
	-1.5	3385			
trans-$[PtCl(PBu_3(PMePh_2)_2]^+$	+9.7	2270		20.0	
	-4.6	3588			
trans-$[PtCl_2(PMePh_2)(SPBu_3)]$ [c]	+55.9		65		6.0
	-3.3	3497			
cis-$[PtCl_2(PMePh_2)(SPBu_3)]$	+53.2		130		
	-3.8	3637			
trans-$[PtCl_2(SPMePh_2)(PBu_3)]$ [c]	+39.9				6.3
	+1.0	3397			
trans-$[Pt_2Cl_4(PMePh_2)(PBu_3)]$	+4.6	3790			
	-14.9	3801			
$[PtClPh(CO)(PMePh_2)]$ (P trans to Cl) (II)	-1.7	3920			
$[PtClPh(CO)(PMePh_2)]$ (P trans to CO) (III)	+5.7	3481			
cis-$[PtPh(CO)_2(PMePh_2)]SO_3CF_3$ [c]	-1.5	3374			
cis-$[Et_4N][PtCl_2Ph(PMePh_2)]$	-1.4	4757			

(a) Recorded in $CDCl_3$ at +30°C unless otherwise stated.

(b) Relative to 85% aqueous H_3PO_4, positive shifts are downfield of standard.

(c) Recorded at -60°C

Experimental:

$^{31}P-\{^{1}H\}$ n.m.r. spectra were recorded on a Varian XL.100 spectrometer operating in the F.T. mode. The complexes $[Pt_2Cl_4(PMe_2Ph)_2]$ $[Pt_2Cl_4(PBu^n_3)_2]$ and $[Pt_2Cl_4(PMePh_2)_2]$ were prepared by standard methods.[71,140] Rapid-mixing experiments were performed by injecting 5ml solutions of $3x10^{-2}$ molar solutions of dimer and phosphine directly into several 5m.m. O.D. n.m.r. tubes (in 0.25ml aliquots) with a tangentially arranged two-jet glass mixing apparatus and capillary. Powdered dry ice was used to cool the equipment and whilst employing $CDCl_3$ solutions the experiments had to be performed quickly (before the solutions froze). In all other experiments $CDCl_3$ solutions of the dimers in 5mm O.D. n.m.r. tubes were cooled to -60°C in an acetone/dry ice slush bath and phosphine (neat or as a solution) was added immediately followed by vigorous agitation of the mixture.

The Reaction of cis-$[Et_4N][PtCl_2(Ph)(PMePh_2)]$ with Carbon Monoxide:

To $[Pt_2Cl_2Ph_2(PMePh_2)_2]$ (20mg ca 20 μmols) dissolved in $CDCl_3$ (0.4mls) was added Et_4NCl (6.5mgs ca 40 μmols) at -60°C to give a solution of cis-$[Et_4N][PtCl_2(Ph)(PMePh_2)]^-$ $\{\delta P$-1.2 ppm $^1J(PPt)4752Hz\}$. As CO was bubbled slowly through the solution at this temperature isomer III was produced. After 25 minutes all $Et_4N[PtCl_2(PMePh_2)Ph]$ was exhausted and no other peaks were noted.

Preparation of $[PtPh(CO)_2(PMePh_2)]SO_3CF_3$ and its Reaction with $Et_4N^+Cl^-$:

A solution $[PtClPh(CO)(PMePh_2)]$ isomers II and III (2% and 98% res-

pectively) was prepared by treating $[Pt_2Cl_2Ph_2(PMePh_2)_2]$ (17mgs 17 μmoles) as a precooled $CDCl_3$ solution (-60°C) with CO for 20 minutes. After adding excess $AgSO_3CF_3$ (40mgs 150 μ mols) treatment with CO was continued for a further 10 minutes to give a solution of cis$[PtPh(CO)_2(PMePh_2)]SO_3CF_3$ $\{\delta(P)$-1.5ppm $^1J(P,Pt)3374Hz\}$. The ^{31}Pnmr spectrum did not change upon warming to room temperature. The solution was filtered directly into a 5mm O.D. n.m.r. tube containing $Et_4N^+Cl^-$ (5.6mgs 33 μ moles) at -60°C, and shaken vigorously. A ^{31}Pnmr spectrum showed II in 100% yield, in the presence of small amounts of $[PtPh(CO)_2(PMePh_2)]SO_3CF_3$.

CHAPTER THREE

THE REACTIONS OF DIHALOBISPHOSPHINE PtII COMPLEXES WITH CARBON MONOXIDE AND ISONITRILES

Chapter 3 - Introduction

Many low energy processes of great synthetic and catalytic value are available to the square planar transition metal complexes, which are common for elements near the end of the transition series. The cis/trans isomerisation of square planar PtII phosphine complexes of the type $[PtX_2L_2]$ {X = halide, L = R_3P} has been the subject of extensive investigations both from the thermodynamic[143] and mechanistic[81-83,135(iii)] viewpoints. An important aspect of ligand catalysed isomerisation reactions concerns the relative thermodynamic stabilities of the mixed ligand species such as $[PtX_2L'L]$ $[PtXL'_2L]^+$ and $[PtXL'L_2]^+$ [82] which might appear either during the L catalysed isomerisation of $[PtX_2L_2]$ or during the L' catalysed transformation of $[PtX_2L_2]$.

The reactions of a variety of $[PtX_2L_2]$ with (i) CO and (ii) CNR {R = Ph,Me} and the influence of reagents such as sulphur and $AgSO_3CF_3$ on the reactions were investigated using ^{31}Pn.m.r. (at -30°C and -60°C), ^{1}Hn.m.r. and infrared spectroscopies with a view to understanding this aspect.

Results and Discussion

During the treatment of chloroform solutions of cis-$[PtCl_2\{P(p\text{-tolyl})_3\}_2]$ with carbon monoxide at room temperature in the presence of excess yellow sulphur, solution infrared spectra (2400-1900cm^{-1}) show the growth of a sharp and very intense terminal metal carbonyl stretching band at 2119cm^{-1} in ca 90 mins. ^{31}Pn.m.r. spectroscopic examination of a similar mixture in $CDCl_3$ exhibit the growth of peaks for

$(\underline{p}\text{-tolyl})_3PS$ and an unknown $\{\delta(P)+8.2$p.p.m., $^1J(P,Pt)$ 3043Hz$\}$ in equal intensity as starting material is consumed. The unknown is assigned as $\underline{cis}$-$[PtCl_2(CO)\{P(\underline{p}\text{-tolyl})_3\}]$ after comparing its infrared and n.m.r. spectroscopic parameters with those of $\underline{cis}$-$[PtCl_2(CO)\{P(\underline{o}\text{-tolyl})_3\}]$ $\{\nu(CO)2110cm^{-1}$. $\delta(P)$ + 5.6p.p.m. $^1J(P,Pt)$ 3010Hz$\}$.[144] $\underline{Cis}$-$[PtCl_2\{P(\underline{p}tolyl)_3\}_2]$ does not carbonylate at all under similar conditions in the absence of sulphur. The overall reaction in the presence of sulphur is summarised in equation (1).

$$\underline{cis}\text{-}[PtCl_2\{P\underline{p}\text{-tolyl})_3\}_2] \xrightarrow[CHCl_3]{CO,XsS_8} \underline{cis}\text{-}[PtCl_2(CO)\{P(\underline{p}tolyl)_3\}] + SP(\underline{p}\text{-tolyl})_3 \qquad (1)$$

In order to investigate both the scope of this extremely useful reaction, and the reaction pathway itself, several examples of the complexes $[PtX_2L_2]$ $\{X$ = halide, L = tertiary phosphine$\}$ as 0.02 molar $CHCl_3$ solutions were treated with CO in the presence of excess sulphur (usually a tenfold excess). The $[PtX_2L_2]$ treated thus are: $\underline{cis}$-isomers, X = Cl, L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, $L_2 = Ph_2P(CH_2)_n$-PPh_2 $\{n = 1.2\}$ X = Br, L = PMe_2Ph; $\underline{trans}$-isomers, X = Cl, L = $P(C_6F_5)_3$, $P(\underline{o}\text{-tolyl})_3$, PPr^i_3, PCy_3, PBu_3, PEt_3, X = Br, L = $P(C_6F_5)_3$, X = I, L = $P(C_6F_5)_3$, PPh_3.

Solution infrared spectra of these mixtures ($2400cm^{-1}$-$1900cm^{-1}$) show the growth in varying rates of $\nu(CO)$ in the region 2103-$2135cm^{-1}$. Only in those cases of $\underline{trans}$-$[PtCl_2L_2]$ $\{L = P(C_6F_5)_3$ and $P(\underline{o}\text{-tolyl})_3\}$ and the chelate diphos complexes are no terminal carbonyl species noted. This may in part be attributable to the poor solubility of these complexes in chloroform. On the basis of the intensities of carbonyl absorptions obtained in these experiments (after 2 hours)

it is possible to construct a table in order of decreasing intensity of absorption. This is only a qualitative description of the processes and its merits and demerits will be discussed later in this chapter. Table 3.

The first indication that the overall carbonylation process, and in turn the above results, cannot be simple were obtained from a preparation scale experiment designed to produce cis-$[PtCl_2(CO)(PEt_3)]$ from a cis-trans $[PtCl_2(PEt_3)_2]$ mixture (1:1). After bubbling CO through the $[PtCl_2(PEt_3)_2]/XsS_8/CHCl_3$ mixture for six hours a very intense $\nu(CO)$ at $2103cm^{-1}$ appeared, suggesting that the reaction had gone to completion. A ^{31}Pn.m.r. spectrum in $CDCl_3$ of the solution residue, however, showed only 20% carbonylation to cis-$[PtCl_2(CO)(PEt_3)]$ and Et_3PS, no other products, and a higher concentration of cis- than trans-$[PtCl_2(PEt_3)_2]$. A chloroform solution of $[PtCl_2(PEt_3)_2]$ treated with CO in the absence of sulphur shows that same $\nu(CO)$ at $2103cm^{-1}$ after one hour. Clearly the strong infrared absorption noted in the sulphur experiment is a composite feature, due to cis-$[PtCl_2(CO)(PEt_3)]$ and some other presumably unstable platinum-carbonyl complex which loses CO upon solvent removal.

^{31}Pn.m.r. spectra taken before and after treating a $CDCl_3$ solution of $[PtCl_2(PEt_3)_2]$ {4:1 trans:cis} with CO for 30 minutes are important for three factors. (i) During the 3 hours at room temperature before treating the sample with CO, the isomer ratio was unchanged, therefore in 30 minutes the solvent alone does not cause appreciable isomerisation. (ii) The final trans:cis isomer ratio after treating with CO for 30 minutes was 0.14:1, $\frac{1}{30}$ of the initial value, therefore the isomerisation has been effected by the CO. (iii) Present as 5% of the total signal

TABLE 3

Comments and Observations of $[PtX_2L_2]$ Carbonylations in Decreasing Order of Reactivity in the Presence of Sulphur

Geometry	X	L	$\nu(CO)^{(a)}_{cm^{-1}}$	Comments
cis	Cl	P(p-tolyl)$_3$	2119	carbonylates fully to (p-tolyl)$_3$PS and cis-$[PtCl_2(CO)\{P(p\text{-tolyl})_3\}]$ in two hours
trans	I	PPh_3	2110	
trans	Cl	PBu^n_3	2108	crude
trans	Cl	PEt_3	2103	4:1 trans:cis - changed in colour from yellow to colourless
cis	Br	PMe_2Ph	2109	
cis	Cl	PEt_3	2103	8:1 cis:trans, became colourless
trans	I	$P(C_6F_5)_3$	2116	a weaker broader $\nu(CO)$ appears at 2108cm^{-1}
cis	Cl	PEt_3	2103	pure cis
cis	Cl	PPh_3	2120	
trans	Br	$P(C_6F_5)_3$	2125	small broad $\nu(CO)$ at 2115cm^{-1}
trans	Cl	PCy_3	2135	
trans	Cl	PPr^i_3	2106	
cis	Cl	$PMePh_2$	2100	
cis	Cl	PMe_2Ph	2114	$\nu(CO)$ small after 2 hours
	Cl	dpe (b)(c)		no visible changes in infrared spectra during prolonged exposure to CO and S_8
	Cl	dpm (b)(c)		
trans	Cl	$P(C_6F_5)_3$ (c)		
trans	Cl	P(o-tolyl)$_3$ (c)		

(a) as 0.02 molar $CHCl_3$ solutions in 0.5mm spacing solution cells.

(b) dpe = 1.2 bisdiphenylphosphinoethane: dpm = 1.2 bisdiphenylphosphinomethane

(c) insoluble.

intensity was the resonance δP+23.5 ppm., $^{1}J(P,Pt)$ 1922 Hz, which infrared data indicate as belonging to a carbonyl complex.

Solution infrared spectra of $[PtCl_2(PEt_3)_2]$ treated with CO in the presence of one equivalent of $AgSO_3CF_3$ (to remove displaced Cl^- as AgCl) show a very intense and sharp ν(CO) at 2103cm^{-1} after ten minutes. A ^{31}Pn.m.r. spectrum of this mixutre contains only one signal {δ(P)+ 26.3 p.p.m. and $^{1}J(P,Pt)$ 1846Hz} which is very similar to the suspected platinum carbonyl. The small P,Pt couplings of these unknowns favour a trans- configuration of phosphines in a complex obtained from $[PtCl_2(PEt_3)_2]$ by the displacement of Cl^- by CO ($AgSO_3CF_3$ evidence). Accordingly these unknowns are assigned as the chloride and $(SO_3CF_3)^-$ analogues of trans-$[PtClCO(PEt_3)_2]^+$. Undoubtedly salts of this type are important intermediates in the isomerisation and carbonylation sequences in chloroform. Similar observations were recorded for the reactions of cis-$[PtCl_2(PMe_2Ph)_2]$ and cis-$[PtCl_2(PMePh_2)_2]$, although less intense ν(CO) were obtained in the absence of sulphur and $AgSO_3CF_3$, and ^{31}Pn.m.r. paramaters were only obtainable for the 'triflate' analogues of the carbonyl cations.

To further test the possible intermediacy of salts such as this in the overall reaction scheme, seven ionic carbonyl species were prepared as $CDCl_3$ solutions using the same method, equation (2).

trans-$[PtX(CO)L_2]SO_3CF_3$, X = Cl:

$$[PtX_2L_2] + CO + AgSO_3CF_3 \xrightarrow{-AgCl} \text{trans-}[PtX(CO)L_2]SO_3CF_3 \qquad (2)$$

L = PMe_2Ph, $PMePh_2$, P(p- tolyl)$_3$, X = Br, L = PMe_2Ph, X = I, L= PPh_3 and $[PtCl(CO)(dpe)]SO_3CF_3$. {dpe = 1,2 bisdiphenylphosphineoethane}. Their vibrational and n.m.r. parameters are given in Tables 4 and 5.

TABLE 4

Spectroscopic Parameters of $[PtX(CO)L_2](SO_3CF_3)$

Complex X	L	Geometry	$\delta(P)^{(a)}$/p.p.m.	$^1J(P,Pt)$/Hz	$^2J(P,P)$/Hz	$\nu(CO)^{(b)}_{cm^{-1}}$
Cl	PEt_3	trans	+26.3	1846		2103
Cl	PEt_3	trans(c)	+23.5	1922		2103
Cl	PEt_3	cis(d)	+18.1d	2776	18.2	____
			+17.2d	2919		
Cl	PMe_2Ph	trans	-1.4	1910		2118
Cl	PMe_2Ph	cis(d)	-9.5d	2925	21.3	____
			-15.0d	3088		
Br	PMe_2Ph	trans	-5.9	1904		2106
Cl	$PMePh_2$	trans	+9.1	1983		2118
Cl	$PMePh_2$	cis(d)	+3.6d	2960	19.5	____
			-8.6d	3162		
I	PPh_3	trans	+18.8	2019		____
Cl	P(p-tolyl)$_3$	trans	+17.8	1959		2115
I	$P(C_6F_5)_3$	trans	-35.8	1929		2095
Cl	dpe (e)	———	+49.3d	——(f)	8.1	2116
			+44.4d	3182		

(a) Recorded in $CDCl_3$ relative to 85% H_3PO_4, positive shifts are downfield.

(b) Measured as 0.02 molar $CHCl_3$ solutions in 0.5mm spacing NaCl window solution cells.

(c) This is trans-$[PtCl(CO)(PEt_3)_2]Cl$

(d) Recorded at -60°C

(e) dpe = 1.2 bisdiphenylphosphinoethane

(f) Not resolved

TABLE 5

Miscellaneous N.M.R. data for Platinum II Complexes

		$\delta(P)^{(a)}$/p.p.m.	$^1J(P;Pt)^{(b)}$/Hz
$[Pt_2(\mu\text{-}Cl)_2L_4]SO_3CF_3$ L =	PEt_3 (c)	+18.6	3537
	PMe_2Ph (d)	-10.6	3793
	$PMePh_2$	+0.7	3795
	$P(p\text{-tolyl})_3$ (d)	+4.0	4078
	dpe	+35.9	3978

	$\delta(H)^{(e)}$/p.p.m.	$^3J(Pt,H)$/Hz	"$J(P,H)$"$^{(f)}$/Hz
trans-$[PtCl(CO)(PMePh_2)_2]SO_3CF_3$	2.55	24.7	11.4
trans-$[PtCl(CO)(PMe_2Ph)_2]SO_3CF_3$	2.15	26.0	9.0

(a) Recorded in $CDCl_3$ at +30°C (or -60°C, note (c)) relative to 85% H_3PO_4 positive shifts are downfield.

(b) No resolved fine structure, i.e. $^3J(P,Pt)$ $^4J(P,P)$ etc.

(c) Recorded at -60°C.

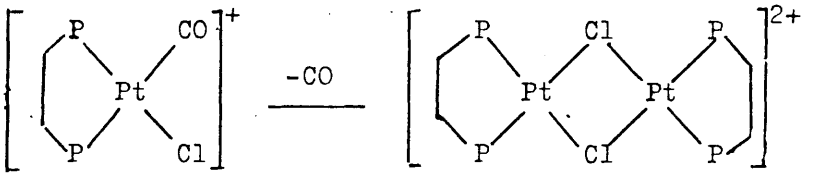
(d) Only approximate $\delta(P)$ and J because the resonances are broad.

(e) Relative to T.M.S. in $CDCl_3$.

(f) This is $|^2J(P,H) + {}^4J(P,H)|$.

The PMe_2Ph and $PMePh_2$ derivatives, show virtually coupled phosphine methyl signals which are triplets of triplets due to the second order coupling $|^2J(P,H) + {}^4J(P,H)|$ and $^3J(Pt,H)$ $\{^{195}Pt\ I = \frac{1}{2}\ 33\%\}$, thus confirming their trans configuration. Attempts to prepare trans-$[PtX(CO)\{P(C_6F_5)_3\}_2]SO_3CF_3$ from trans-$[PtX_2\{P(C_6F_5)_3\}_2]$ $\{X = Cl,Br,I\}$ were unsuccessful, although in each case dramatic colour changes were effected. Only in the case X = I was an intense $\nu(CO)$ recorded ($2095cm^{-1}$), but this did not survive long enough for further infrared analysis. ^{31}Pn.m.r. spectra of the mixture showed largely starting material and a new peak in low concentration $\{\delta(P)$ -35.8 p.p.m. and $^1J(P,Pt)1929Hz\}$ which is assigned to trans-$[PtI(CO)\{P(C_6F_5)_3\}_2]SO_3CF_3$. Dark precipitates were apparent in all three cases after the colour changes, from yellows and oranges to darker colours, later paled.

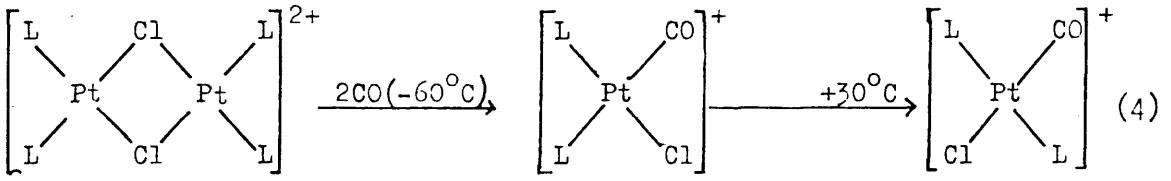
The chelate diphos salt tended to lose CO readily and convert to the very insoluble halide bridged dimeric complex $[Pt_2(\mu\text{-}Cl)_2(dpe)_2](SO_3CF_3)_2$ $\{\delta(P) = 35.9,\ ^1J(P,Pt)\ 3975Hz\}$ equation (3),



(3)

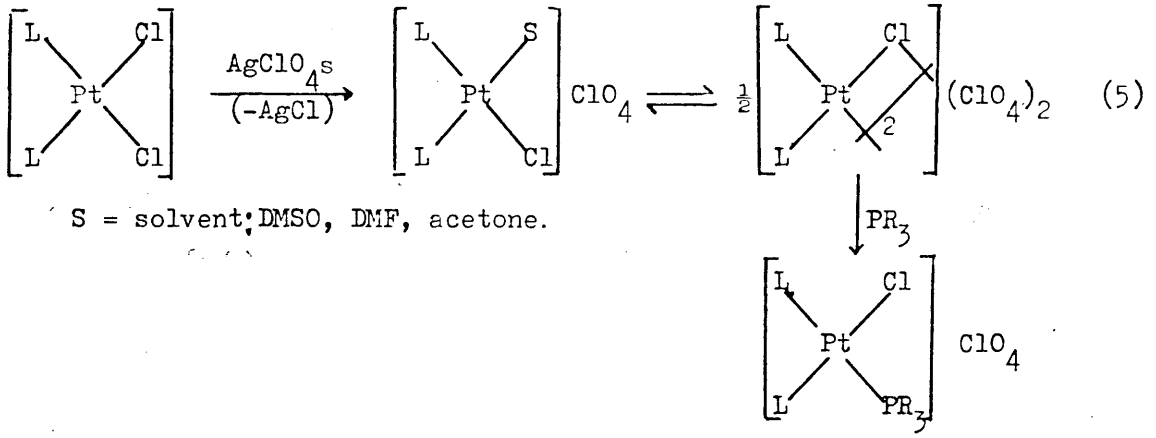
which was reluctant to react with CO to regenerate the monomer, (no doubt because of its insolubility). The reaction of cis-$[PtCl_2(PMePh_2)_2]$ with $AgSO_3CF_3$ and then CO in $CDCl_3$ was investigated at -60°C. At room temperature mixtures of the monomeric complex and $AgSO_3CF_3$ form a single species $\{\delta(P)$ + 0.1 p.p.m. $^1J(P,Pt)$ 3816Hz$\}$. When this species reacts with CO at -60°C it produces a cis bis phosphine complex $\{\delta(P)$ + 3.6 p.p.m.d $^1J(P,Pt)$ 2960Hz, $\delta(P)$-8.6 p.p.m.d $^1J(P,Pt)$ 3162Hz, d $^2J(P,P)$ 19.5Hz$\}$ which on warming periodically to + 30°C for

a few minutes and then cooling converts in stages to trans-$[PtCl(CO)(PMePh_2)_2]SO_3CF_3$. These unknown species are assigned as $[Pt_2Cl_2(PMePh_2)_4](SO_3CF_3)_2$ and cis-$[PtCl(CO)(PMePh_2)_2]SO_3CF_3$, (the carbonyl complex being the cleavage product of the dimer, equation (4)). Their spectroscopic parameters compare favourably with the diphos analogues.



(4)

Similar products have been reported[146] by Hartley et al, using $AgClO_4$ in strongly donating solvents to produce bis-chelate ligand halide bridged PtII and PdII dimers, which were cleaved with tertiary phosphine (equation 5).



(5)

S = solvent; DMSO, DMF, acetone.

Entirely analogous results are observed for the reaction of cis-$[PtCl_2(PMe_2Ph)_2]$ and $[PtCl_2(PEt_3)_2]$ (1:1 cis:trans) with $AgSO_3CF_3$ and CO, and cis-$[PtCl(CO)(PMe_2Ph)_2]SO_3CF_3$ persists at +30°C for several hours. The dimeric complex $[Pt_2(\mu\text{-}Cl)_2(P\text{-}p\text{-tolyl})_3]_4(SO_3CF_3)_2$ is detected in mixtures of cis$[PtCl_2\{P(p\text{-tolyl})_3\}_2]$, CO and $AgSO_3CF_3$ in $CDCl_3$ at room temperature, and its resonance is broad, as are the signals of the PEt_3, $PMePh_2$ and PMe_2Ph derivatives when cis-$[PtCl_2L_2]$ are present. However, these signals sharpen at -60°C.

In a separate line of enquiry it was observed that ^{31}Pn.m.r. signals for $[PtCl_2L_2]$ and $[Pt_2Cl_2L_4](SO_3CF_3)_2$ (1:1) produced by adding 0.5 equivalents of $AgSO_3CF_3$ (L = $PMePh_2$, PEt_3) broadened together at +30°C but sharpened considerably at -60°C. Excess $AgSO_3CF_3$ produces sharp signals for the dimer alone at room temperature.

For a 1:1 cis:trans mixture of $[PtCl_2(PEt_3)_2]$ and $[Pt_2Cl_2(PEt_3)_4](SO_3CF_3)_2$ at +30°C only the ^{31}P resonance of the trans isomer is sharp. Clearly halide exchange, rapid at +30°C and slow at -60°C, is responsible for the broadened lines at the higher temperature and this exchange is exclusively between $[Pt_2Cl_2L_4](SO_3CF_3)_2$ and cis-$[PtCl_2L_2]$.

Halide for the exchange is probably made available by its displacement of Cl^- from cis-$[PtCl_2L_2]$ by solvent ($CHCl_3$), (equation 6) which, in view of

$$\text{cis-}[PtCl_2L_2] \underset{-S}{\overset{+S}{\rightleftharpoons}} [PtCl(S)L_2]^+ + Cl^- \qquad (S = \text{solvent}) \qquad (6)$$

the sharpness of the phosphorus resonances of $[PtCl_2L_2]$ at room temperature is easily displaced by Cl^- (i.e. the equilibrium lies well to the left). Whether Ag^+ abstracts a coordinated halide or reacts with the ionic chloride, to give AgCl, the presumed solvento complex thus formed dimerises rapidly to give $[Pt_2Cl_2L_4](SO_3CF_3)_2$ because such solvento complexes are not observed even at -60°C. Equilibrium (6) is now displaced by the dimeric complex (which probably reacts with Cl^- by a factor of 10^3 times that of monomer)[122] and cis-$[PtCl_2L_2]$ is produced. In this way exchange broadened phosphorus signals appear. The metal halide bonds in cis-$[PtCl_2L_2]$ {L = PR_3} are longer and weaker than those in the trans- isomer,[24] and consequently more easily displaced by solvent. This aspect alone may account for the exclusivity of exchange between $[Pt_2Cl_2L_4]^{2+}$ and the cis- isomer of $[PtCl_2L_2]$.

The cationic dimers are cleaved by CO to give exclusively cis-$[PtCl(CO)L_2]SO_3CF_3$ which isomerises to the trans form upon warming to $+30^oC$ in the presence of excess CO. Solvent and/or CO may be involved in the isomerisation, which is irreversible.

The products from the reactions of the salts trans-$[PtX(CO)L_2]SO_3CF_3$ with halide X^- in the presence of excess sulphur are important to considerations of the course of both the isomerisation and the carbonylation sequences. The only products observed in the reaction of trans-$[PtX(CO)L_2]SO_3CF_3$ with X^- {X = Cl, L = PMe_2Ph, $PMePh_2$, X = Br, L = PMe_2Ph} are the cis-$[PtX_2L_2]$. The diphos analogue reacts similarly to give $[PtCl_2(dpe)]$. The nonappearance of cis-$[PtX_2(CO)L]$ and phosphine sulphide in these four cases is consistent with a rapid displacement of CO by X^- followed by rapid isomerisation of the probable trans- product to give the observed cis species. (The final step is, of course, unimportant where L_2 = dpe.) The isomerisation step and the CO loss may be more intimately related, i.e. the isomerisation may be effected by the displaced CO. Accordingly the reactions of these cis-$[PtX_2L_2]$ with CO and sulphur (Table 3) are slow because displacement of CO from $[PtX(CO)L_2]^+$ (cis or trans) is rapid.(equation 7).

$$\text{cis-}[PtX_2L_2] \xrightarrow[-CO]{+CO} [PtX(CO)L_2]^+X^- \qquad (7)$$

Varying amounts of trans-$[PtX_2L_2]$ {X = I, L = PPh_3 only}, cis- PtX_2L_2, cis-$[PtX_2(CO)L]$ and LS tertiary phosphine sulphide are produced from the reactions of trans-$[PtX(CO)L_2]$ SO_3CF_3 {X = Cl, L = PEt_3, P(p-tolyl)$_3$, X = I, L = PPh_3} with X^- {$Et_4N^+Cl^-$ or $Bu^n{}_4NI$}. (Table 6)

These results do not parallel those data obtained from infrared examination of the $[PtX_2L_2]/CO/S_8$ mixtures (displayed in Table 3) and this is puzzling.

Table 6

Products of the reactions of $[PtX(CO)L_2]^+$ with X^-

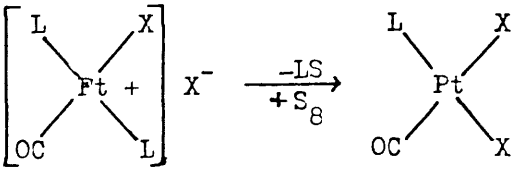
X	L	$[PtX_2L_2]$ (%)[a] cis	trans	cis-$[PtX_2(CO)L]$ (%)	LS(%)	Others
Cl	PEt_3	70	5	10	10	5 [b]
Cl	$P(p\text{-tolyl})_3$	44	—	11	28	17 [b]
I	PPh_3	—	32	32	32	4 [b]

(a) Calculated from ^{31}P signal intensities and so these are approximate.

(b) Unknown resonances.

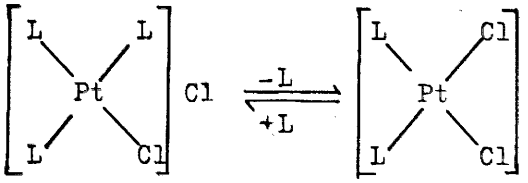
It is conceivable that the nature of the reaction of the displaced phosphine with the sulphur (that is present largely as a suspension) is critically dependent upon the extent of agitation of the reaction mixtures, and this is difficult to standardise.

Despite this anomaly these experiments serve to illustrate the restricted range of products obtained. The comparable amounts of phosphine sulphide and cis-$[PtX_2(CO)L]$ fit mass balance requirements (in two cases at least) and the stereochemistry of the carbonyl complex strongly suggests that they may be formed in the same step (equation 8).



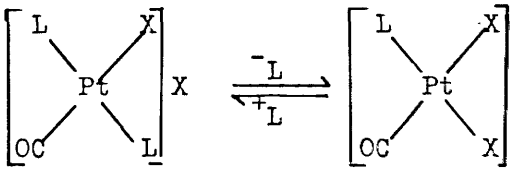
(8)

The rapid room temperature ligand exchange between $[PtCl(PMe_2Ph)_3]Cl$ and cis-$[PtCl_2(PMe_2Ph)_2]$ reported[82] from ^{1}Hn.m.r. evidence (equation 9) is explained in terms of a consecutive displacement mechanism.



$L = PMe_2Ph$ (9)

L displaces Cl^- (trans to L) in cis-$[PtCl_2L_2]$, and Cl^- displaces L (trans- to L) in $[PtClL_3]^+$ exclusively (and not L trans to Cl^-). We propose that trans-$[PtX(CO)L_2]^+$ in some cases reacts with X^- in an analogous manner: X^- displaces L (trans to L) in $[PtX(CO)L_2]^+$ (and not CO trans to X) to give cis-$[PtX_2(CO)L]$. This displacement is irreversible upon the formation of the phosphine sulphide. As has been shown CO loss does occur to some extent in these cases (Table 6), and in earlier cases total CO loss has been effected. These observations are consistent with an equilibrium such as (9) which operates in competition with a second reaction involving loss of CO (equation 10). Whilst in some cases the side reaction predominates



$\longrightarrow [PtX_2L_2]$ (10)

in others an intermediate state of affairs exists.

Scheme I depicts a probable mechanistic explanation, given the evidence from the reactions of trans-$[PtX(CO)L_2]SO_3CF_3$ with X^-, the possible effect of solvent on the exchange broadening phenomenon observed in mixtures of $[Pt_2X_2L_4](SO_3CF_3)_2$ and cis-$[PtCl_2L_2]$, and the certain possibility of intermediate cis-$[PtX(CO)L_2]^+$ species at room temperature, which isomerise rapidly in the presence of excess CO. Several important factors may be summarised as follows:-

(i) In view of the cis monomer-dimer ligand exchange process, solvent assisted carbonylation is unlikely from trans-$[PtX_2L_2]$ which does not interconvert with the dimer.

(ii) The differences in the n.m.r. parameters of trans-$[PtCl(CO)(PEt_3)_2]$ SO_3CF_3 and its chloride analogue are suggestive of anion-cation interaction, perhaps to form a species like A of Scheme I.

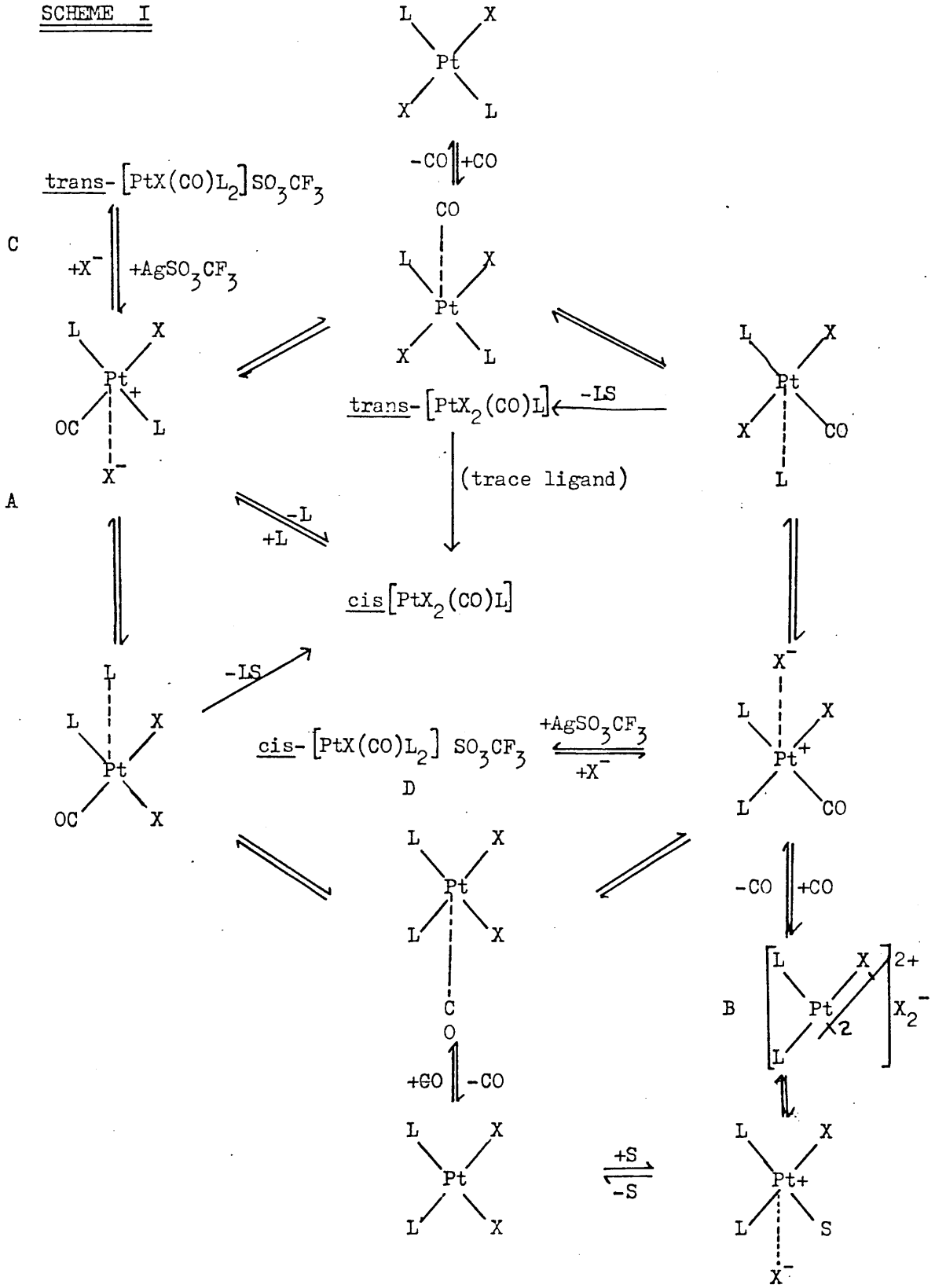
(iii) The individual steps between the recognised intermediates A,B,C and D ($X^- = SO_3CF_3$) and the others (which are unlabelled) may possibly proceed via trigonal bipyramidal transition states.

(iv) An alternative route to cis-$[PtX_2(CO)L]$ via the trans-isomer must be considered, particularly in view of the already observed facile isomerisation of trans-$[PtX_2(CO)L]$ by a variety of free ligands.[144] The trans- isomer was not detected at any stage.

(v) The yellow sulphur serves to 'mop up' displaced tertiary phosphine (L) certainly in those cases of interconversion between trans-$[PtX(CO)L_2]^+X^-$ and cis-$[PtX_2(CO)L]$, and possibly in two other instances, as indicated.

On examining Table 3 we can use particular cases to illustrate the overall carbonylation process if we rely on these particular instances as being typical examples. The carbonylation process is critically dependent on the phosphine, and on the whole the triaryl phosphine complexes react more readily than the trialkyl phosphine derivatives. Electron donating substituents on the aryl- portions of those phosphines accelerate carbonylation (compare P(p-tolyl)$_3$ and PPh_3). However, the (o-tolyl)$_3$P complex, either as a result of poor solubility or of steric overcrowding, was not carbonylated. Trans-$[PtX_2L_2]$ reacts faster than the cis-isomer {X = Cl, L = PEt_3}, and the bromide derivatives more rapidly than the chlorides, for the same phosphine,

SCHEME I


trans-[PtX(CO)L2]SO3CF3
C
+X⁻
+AgSO3CF3
-CO
+CO
trans-[PtX2(CO)L]
-LS
(trace ligand)
A
-L
+L
cis[PtX2(CO)L]
-LS
cis-[PtX(CO)L2] SO3CF3
+AgSO3CF3
+X⁻
D
+CO
-CO
B
2+
X2⁻
+S
-S

and geometry { cis-$[PtX_2(PMe_2Ph)_2]$ X = Br, Cl}. Finally the diphos analogues lose CO readily and do not form any carbonyl complexes (except with $AgSO_3CF_3$), perhaps because the salts cannot isomerise to a more thermodynamically favourable trans-form.

Until the reactions of a wider range of $[PtX_2L_2]$ with CO and sulphur have been investigated, particularly of chloride, bromide and iodide derivatives of the same phosphine and geometry, the trends suggested must be regarded as partly speculative. As has been discussed not all of the ν(CO) in Table 3 are due to cis-$[PtX_2(CO)L]$. The carbonyl peaks obtained from trans-$[PtX_2\{P(C_6F_5)_3\}_2]$, CO and S_8 cannot be due to ionic complexes, and cannot be attributed the reaction of $P(C_6F_5)_3$ and S_8, which is infinitely slow in comparison.[148] Candidates for the absorption bands include cis and trans-$[PtX_2(CO)L]$ and/or a five coordinate complex $[PtX_2(CO)L_2]$.

Attempts to establish the synthetic utility of the CO/S_8 treatment were not successful owing to the difficulty of removing the tertiary phosphine sulphide from solutions of the cis-$[PtX_2(CO)L]$, { X = Cl, L = PEt_3, PBu^n_3, PPh_3 and P(-tolyl)$_3$}. A 20% yield of cis-$[PtCl_2(CO)(PBu_3)]$ was obtained by chromatographic separation, but the bulk of the product was cis-$[PtCl_2(Bu^n_3PS)(PBu^n_3)]$ (80%){ δ(P) - 4.3p.p.m.d ^1J(P,Pt) 3556Hz, δ(P) + 72.3 p.p.m.d ^1J(P,Pt) 125Hz, ^3J(P-P) 16Hz}, no doubt as a result of Bu_3PS displacement of CO from the carbonyl product.

The Reactions of PtII Monomeric Complexes with Isonitriles.

Analogous investigations to those of the carbonylations can be extended

to the reactions of three types of bis (neutral ligand) dichloro PtII complexes with tertiary phosphine, and methyl and phenyl isonitries. These are:-

(i) (a) cis-$[PtCl_2(CNR)_2]$ + $PMePh_2$. R = MePh

(b) cis-$[PtCl_2(CNR)L]$ + CNR. R = MePh

(ii) $[PtX_2L_2]$ + CNR. X = Cl, L = PCy_3, $PMePh_2$, P (ctolyl)$_3$, P(p-tolyl)$_3$ and X = Br, L = PMe_2Ph which are all cis except for PCy_3 and P(otolyl)$_3$ derivative. Only cis-$[PtCl_2(PMePh_2)_2]$ was allowed to react with CNMe and in all cases CNPh was used.

(iii) cis-$[PtCl_2(CNR)L]$ + L : R = Me, L = $PMePh_2$; R = Ph, L = $PMePh_2$, PMe_2Ph and PBu^n_3.

Reactions all carried out in $CDCl_3$ or $CHCl_3$ for either ^{31}P and ^1H n.m.r. or infrared spectroscopies respectively.

The reactions of cis-$[PtCl_2(CNMe)_2]$ with $PMePh_2$ (1:1) and cis-$[PtCl_2(CNMe)(PMePh_2)]$ with CNMe (in $CDCl_3$) are characterised by the same broad phosphorus resonance at δ(P) - 7.5p.p.m. (J(P,Pt) ca 2800Hz) which occurs in both cases. This is prevalent after 20 days in each case, and sharp signals are apparent as well, although they are different: cis-$[PtCl_2(CNMe)(PMePh_2)]$ is the other product in the first reaction and an unknown {δ(P) - 2.74 p.p.m. ^{1}J(P,Pt) 2433Hz } appears in the second case. Whilst phosphine exchange would cause collapse of the satellites due to ^{31}P — ^{195}Pt (I = $\frac{1}{2}$, 33%) coupling, CNMe exchange would only broaden them as much as the central resonances. Clearly it is the latter process which operates here.

^{1}Hn.m.r. spectra of both these reactions are identical, but apart from aromatic-H resonances only two other signals at δ(H) 3.45 p.p.m.

and 2.62 p.p.m. (both broad) are apparent. These signals correspond to isonitrile and phosphine methyl protons respectively. The unknown resonance is not due to trans-$[PtCl_2(CNMe)(PMePh_2)]$ (Chapter 4) nor is it typical of trans-$[PtCl(CNMe)(PMePh_2)_2]^+$ (vide infra), but considering the stoichometry of the reaction it could be due to $[PtCl(CNMe)_2(PMePh_2)]^+$. This cis isomer is the more likely candidate because like the mutually trans-phosphines in $[PtCl(PMe_2Ph)_3]^+$ it has a similar $^1J(P,Pt)$. P trans to Cl have J(P,Pt)'s which are generally >3000Hz.

Without more detailed spectroscopic examinations of these experiments any questions about the nature of the complexes involved in the exchange broadened ^{31}P resonance must remain unanswered.

In contrast to the above examples no broadening phenomena were noted during the reaction of cis-$[PtCl_2(CNPh)_2]$ with neat $PMePh_2$ in $CDCl_3$ at room temperature. Of the eight ^{31}P resonances observed ten minutes after mixing, only four are known: cis and trans-$[PtCl_2(CNPh)(PMePh_2)]$ 1:1 8%, trans-$[PtCl(CNPh)(PMePh_2)_2]^+Cl^-$ 22%, and a resonance at $\delta(P)$ -3.9 p.p.m. $^1J(P,Pt)$ 2430Hz was noted. This latter signal is similar to the unknown from the reaction of $[PtCl_2(CNMe)L]$ with $L(=PMePh_2)$ 22%. The remaining signals are (i) $\delta(P)$-0.5 p.p.m. J(P,Pt) 2580Hz 33%. (ii) $\delta(P)$ + 0.4 p.p.m. J(P,Pt) 1981Hz 7%. (iii) $\delta(P)$ -4.7 p.p.m. $^1J(P,Pt)$ 3250Hz 7% and (iv) $\delta(P)$ -5.0 p.p.m. no resolved $^1J(P,Pt)$, ca 1%. Bis-phosphine platinum complexes have arisen because of the likely unhomogeneity of mixing conditions, which allow the initial product of $[PtCl_2(CNPh)_2]$ and $PMePh_2$ to react with a further quantity of $PMePh_2$, and possibly leave unreacted starting material.

When left overnight to react further no changes in the product mixture were detected. As in the case of the CNMe reactions it is too difficult to determine the many complex processes that have occured in this reaction, because a large proportion of the products remain unidentified. Solution infrared spectra (2400 - 1900cm $^{-1}$) of this reaction mixture and of $[PtCl_2(CNMe)_2]$ and $PMePh_2$ show the disappearance of the two intense ν(NC) of the isonitrile complex reactants and its replacement by broad but intense isonitrile bands at 2265cm $^{-1}$ ($CNCH_3$) 2225cm $^{-1}$ (CNPh) respectively.

The reactions of several $[PtX_2L_2]$ with phenyl-isonitrile (and in one case with CNMe) are analogous to those carbonylations mentioned before, which involve the effective substitution of tertiary phosphine with CO that is accomplished with the aid of sulphur crystals. ^{31}Pn.m.r. spectroscopic studies have shown the range of products for these reactions to be diverse. Amongst them however are the ionic complexes trans-$[PtX(CNR)L_2]^+X^-$ {X = halide, R = Ph, L = tertiary phosphine} which are more stable than the carbonyl analogues in the presence of a coordinating anion. Tertiary phosphine (L) reacts cleanly and rapidly with cis-$[PtCl_2(CNR)L]$ (reaction type (iii)) to give only trans-$[PtCl(CNR)L_2]^+Cl^-$. The processes involved are complete prior to spectroscopic analysis (a few minutes at most).

Spectroscopic data for $[PtX(CNR)L_2]^+Y^-$ {Y = Cl or SO_3CF_3, R = Me, X = Cl, L = $PMePh_2$; R = Ph, X = Cl, L = PMe_2Ph, $PMePh_2$, PBu^n_3, PCy_3, X = Br, L = PMe_2Ph} are given in Table 7. All of the complexes have small ^1J(P,Pt) values in the range 1967 - 2148cm $^{-1}$ and ^{1}Hn.m.r. spectra of the methyl-phosphine derivatives show the second order feature of virtual coupling which proves their trans- geometry. ^{1}Hn.m.r. parameters

of trans-$[PtCl(CNR)(PMePh_2)_2]^+Cl^-$ are given in Table 8.

When $CDCl_3$ solutions of $[PtX_2L_2]$ {X = Cl, L = $PMePh_2$, PMe_2Ph, both cis, and L = PCy_3, P(o-tolyl)$_3$ both trans} are mixed with one equivalent of CNPh in the presence of $AgSO_3CF_3$ (1.2 equivalents) at room temperature, these trans $[PtX(CNR)L_2)]SO_3CF_3$ are the major products in the first three cases, whilst a P(o-tolyl)$_3$ analogue was not identified. Solution infrared spectra did show a sharp $\nu(N\equiv C)$ at 2192cm^{-1} for this case, but a ^{31}Pn.m.r. spectrum of the mixture showed six peaks, of which only one could be tentatively assigned as trans-$[PtCl_3\{P(o\text{-tolyl})_3\}_2]$ {δ(P)+ 20.9 p.p.m. ^1J(P,Pt) 2661Hz}.

Two of these experiments were repeated in the absence of $AgSO_3CF_3$ and examined by ^{31}Pn.m.r. spectroscopy. Cis-$[PtCl_2L_2]$ {L = $PMePh_2$, PMe_2Ph} and CNPh in $CDCl_3$ at ambient temperature give very broad resonances which persist for 40 days before detectable amounts of trans-$[PtCl(CNPh)L_2]^+Cl^-$ appear. The solutions brown considerably, presumably as a result of displaced CNPh oligomerisation, and copious quantities of the cis-starting materials are regenerated as the exchange phenomena dissipate.

In the presence of excess sulphur cis$[PtX_2L_2]$ {X = Cl L = P(p-tolyl)$_3$ and X = Br L = PMe_2Ph} react with CNPh at +20°C in $CDCl_3$ to give varying quantities of cis-$[PtX_2(CNPh)L]$ and phosphine sulphide (1:1). The P(p-tolyl)$_3$ complex gives only two products which are SP(p-tolyl)$_3$ +42.4 p.p.m. and cis-$[PtCl_2(CNPh)\{P(p\text{-tolyl}_3)\}]$[$\delta$(P) +6.7 p.p.m. ^1J(P,Pt) 3347Hz (equation 11). The bromide complex has the analogous sulphide and cis-complex as 77% of its

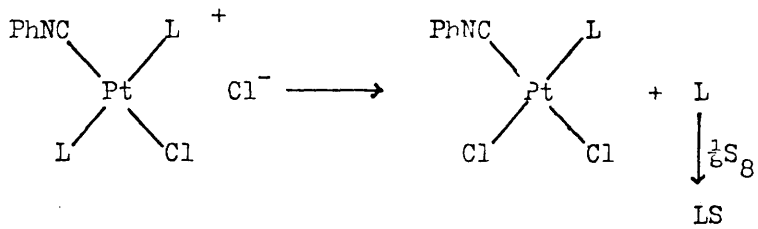
$$\text{cis-}[PtCl_2\ P(p\text{-tolyl})_3]_2 + CNPh \xrightarrow[CHCl_3]{\frac{1}{8}S_8} \text{cis-}[PtCl_2(CNPh)\{P(p\text{-tolyl})_3\}] + SP(p\text{-tolyl})_3 . \quad (11)$$

products which also include trans-$[PtBr_2(PMe_2Ph)_2]$ (4%), a resonance at δ(P) -8.24 p.p.m. ^1J(P,Pt) 2060Hz which is tentatively assigned to trans-$[PtBr(CNPh)(PMe_2Ph)_2]Cl$ (9%), and an unknown {δ(P) -16.1 p.p.m. ^1J(P,Pt) 2425Hz}.

Solutions of trans-$[PtCl(CNPh)L_2]Cl$ {L = PMe_2Ph, $PMePh_2$, PBu^n_3} convert exclusively to cis-$[PtCl_2(CNR)L]$ and LS in the presence of excess sulphur at room temperature over periods of several hours. ^{31}Pn.m.r. spectra of trans-$[PtCl(CNPh)(PMePh_2)_2]SO_3CF_3$ (obtained by shaking the chloride derivative with excess $AgSO_3CF_3$ and filtering), remained unchanged for several hours in the presence of sulphur until excess $Et_4N^+Cl^-$ was added to the system, whereupon it behaved in the same manner as the chloride derivative (equation 12). Presumably as in Cooper and Powell's studies[82] on $[PtCl(PMe_2Ph)_3]^+Cl^-$ it is

$$\text{trans-}[PtCl(CNPh)L_2]Cl \xrightarrow{\frac{1}{8}S_8} \text{cis-}[PtCl_2(CNPh)L] + LS \qquad (12)$$

halide displacement of phosphine trans to phosphine in trans-$[PtCl(CNPh)L_2]Cl$ which produces solely cis-$[PtCl_2(CNPh)L]$ and free $PMePh_2$ (and this is subsequently oxidised) that is the key step in this reaction (equation 13).

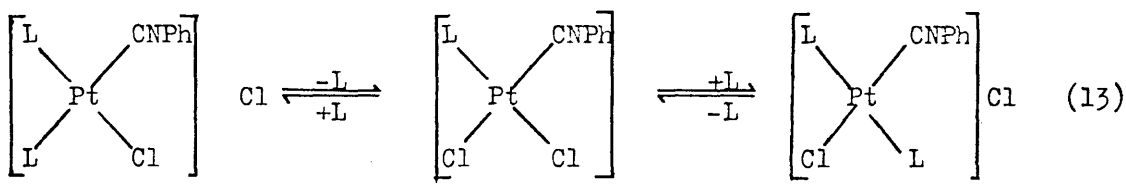


(13)

The phosphine oxidation step presumably displaces the equilibrium, which usually lies well to the left, in an analogous manner to the way added $[Pt_2Cl_4(PMe_3)_2]$ affects the equilibrium of $[PtCl(PMe_3)_3]Cl$ with cis-$[PtCl_2(PMe_3)_2]$[84].

Although the salts cis-$[PtX(CNR)L_2]X$ (or SO_3CF_3) were not investigated

it is reasonable to presume (on the evidence of the trans isomers) that they would be as stable (if not more so) than the carbonyl analogues observed as 'triflate' salts, but their stability with respect to isomerisation is unknown. In the absence of an excess of free ligand it could possibly be greater than that of the carbonyl derivatives. If trans-$[PtCl(CNPh)\{P(\underline{p}\text{-tolyl})_3\}_2]Cl^-$ is an intermediate in the reaction of cis $[PtCl_2\{P(\underline{p}\text{-tolyl})_3\}_2]$ with CNPh and S_8 to give cis-$[PtCl_2CNPh\{P(\underline{p}\text{-tolyl})_3\}]$ and $(\underline{p}\text{-tolyl})_3PS$, then it must be consumed more rapidly in the presence of sulphur than the analogous PBu_3, $PMePh_2$ and PMe_2Ph complexes. Whilst the latter are totally converted to cis complex and sulphide in 3-4 hours at +20°C the $P(\underline{p}\text{-tolyl})_3$ reaction is over in 35 minutes. However, if $[PtCl(CNPh)\{P(\underline{p}\text{-tolyl})_3\}]Cl$ also requires 3-4 hours to be consumed a new intermediate that loses phosphine must be postulated. Let this intermediate be cis-$[PtCl(CNPh)L_2]Cl$. It is proposed that in isomerising to the trans- complex, phosphine trans to CNPh is lost to give cis-$[PtCl_2(CNPh)L]$ which in turn reacts rapidly with



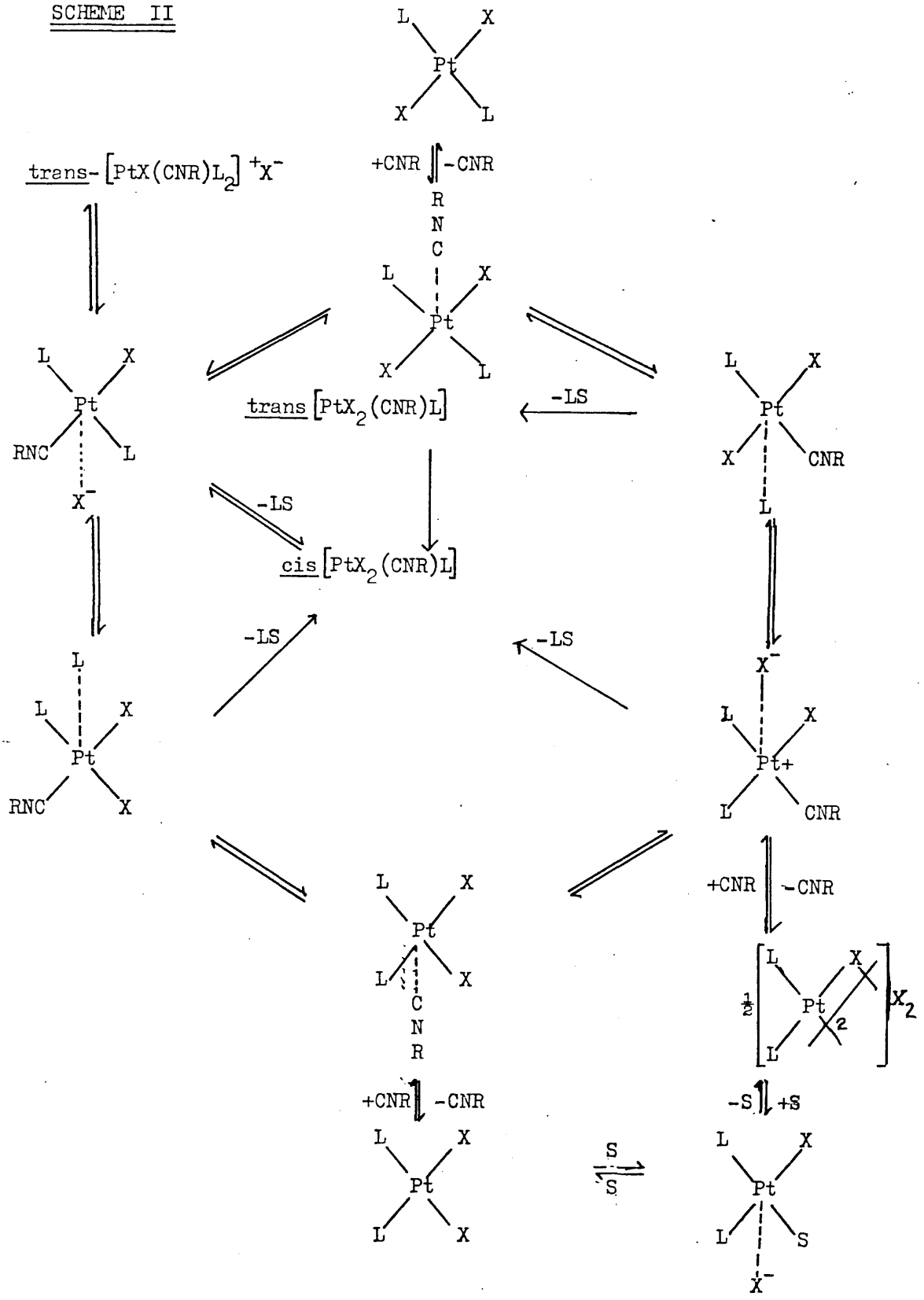
(13)

L to give trans-$[PtCl(CNPh)L_2]Cl$ (equation 13).

It is possible that the first equilibrium of this overall isomerisation process is displaced by oxidation of the released phosphine, as it is for the second equilibrium.

Scheme II is constructed by analogy with Scheme I but it includes the possible extra reaction of an intermediate cis-$[PtX(CNPh)L_2]^-X$ giving cis-$[PtX_2(CNPh)L]$ and LS in the presence of sulphur. Without

SCHEME II


trans-[PtX(CNR)L2]+X-
+CNR
-CNR
RNC
trans[PtX2(CNR)L]
-LS
-LS
cis[PtX2(CNR)L]
-LS
-LS
+CNR
-CNR
+CNR
-CNR
-S
+S
S
S

extensive investigations of the role and significance of a cis or trans-$[PtX(CNR)L_2]X$ in the reaction of $[PtX_2L_2]$ with CNR for a wider range of phosphines, using ambient and low temperature ^{31}Pn.m.r. spectroscopy, Scheme II must remain somewhat speculative.

Experimental

^{31}P ^{1}H n.m.r. spectra were recorded as $CDCl_3$ solutions using a Varian XL100 spectrometer operating in the Fourier Transform mode. ^{1}H n.m.r. spectra were recorded using a Perkin Elmer R32 spectrometer (90MHz). Solution infrared spectra were recorded as 0.02 molar $CHCl_3$ solutions in 0.5mm NaCl cells on a P.E. 577 instrument. Cis and trans$[PtX_2L_2]$ were prepared by literature methods.[24]

$[PtX_2L_2]$ + CO + S_8

Typically 10-20mgs of the$[PtX_2L_2]$ were dissolved (if possible) in sufficient dried $CHCl_3$ to give a 0.02 molar solution ca 1ml in a volumetric flask. An approximate 10 fold excess of yellow sulphur crystals (w.r.t. L) 2-3 mgs were added and CO (dried by passage over silica gel, and sodium alumino silicate type 4A) was applied through a pasteur pipette. The gas bubbles efficiently disturbed the sulphur crystals at all times. Solution infrared spectra of filtered aliquots (0.2mls) were recorded periodically. The total volume of the mixture was maintained at ca 1ml with fresh $CHCl_3$.

Preparation of trans-halo carbonyl bis (tertiary phosphine) platinum Trifluoromethane-Sulphonate : trans-$[PtXCOL_2]^+(SO_3CF_3)^-$

A 0.02 molar solution of$[PtX_2L_2]$ was saturated with CO before one

equivalent of $AgSO_3CF_3$ was added to the mixture. Treatment with carbon monoxide was continued for a further 30-40 minutes and followed to completion by solution infrared spectroscopy. Filtration and removal of the solvent followed by application of deuteriochloroform allowed ^{1}Hn.m.r. and ^{31}Pn.m.r. specroscopic analysis.

Low Temperature Study of Cis-chloro-carbonylbis (methyldiphenylphosphine) platinum Trifluoromethanesulphonate

A $CDCl_3$ solution of cis$[PtCl_2(PMePh_2)_2]$(36.1mgs ca 400 μls $CDCl_3$) in the presence of $AgSO_3CF_3$ (15 mgs) mixed at -60°C were examined by ^{31}Pn.m.r. spectroscopy. Two other species were present, namely $[Pt_2(\mu\text{-}Cl)_2(PMePh_2)_4]^{2+}$ and an unknown at δ(P) -1.0 p.p.m. $^1J(P,Pt)$ 3805Hz present as ca 65% and ca 6% respectively of the total signal intensity. After treating the sample with CO at -60°C for a total of 35 minutes, ^{31}Pn.m.r. spectra had shown the growth of a pair of triplet of doublet resonances (Table 7) as all three previous signals decreased to a negligible intensity (in total 5-10%). By allowing the sample to heat up to room temperature for 2-3 minutes at a time and then cooling it, these doublet resonances decreased in intensity to be replaced by one singlet resonance trans-$[PtClCO(PMePh_2)_2](SO_3CF_3)$ after a total of 8 or 9 minutes. Several days later the same sample in an ambient temperature ^{31}Pn.m.r. spectrum showed only trans-$[PtCl(CO)(PMePh_2)_2]^+(SO_3CF_3)^-$, as being present and no cis isomer.

Preparation of Trans Chloro phenylisonitrile bis (tertiary phosphine) Trifluoromethanesulphonate, and their reactions with S_8

A quantity of cis$[PtCl_2(CNPh)L]$ $\{L = PMe_2Ph, PMePh_2, PBu^n_3\}$ (20-40mgs)

was dissolved in $CDCl_3$ in a 5mm diameter n.m.r. tube and one equivalent of the tertiary phosphine (L) was added neat using a microlitre syringe. ^1H and $^{31}P-\{^1H\}$n.m.r. spectra were recorded, before 10mgs of S_8 were added to the tube and the sample then shaken vigorously, and after 3-4 hours the reaction had proceeded by ca 80% to LS and cis$[PtCl_2(CNPh)(L)]$. In the case of trans$[PtCl(CNPh)(PMePh_2)_2]$ (SO_3CF_3) the chloride was shaken for 2-3 minutes with one equivalent of $AgSO_3CF_3$ and then filtered.

Attempts to isolate trans-$[PtCl(CNPh)(PMePh_2)_2]Cl$ on a preparative scale (2-300mgs) gave dark brown oils from originally colourless solutions as a result of phenyl-isonitrile polymerisation. The SO_3CF_3 analogue gave colourless oils despite attempted recrystallisation from a very wide range of solvents. However, they gave clear and unambiguous ^1H and ^{31}Pn.m.r. spectra and solution and solid infrared spectra. The CNMe derivatives behaved similarly.

CHAPTER FOUR

ISONITRILE COMPLEXES OF PLATINUM (II)

Chapter 4 - Introduction

Isonitriles are among the few substances with a lone pair located on a carbon atom. Their structure is isoelectronic with carbon monoxide and the lone pair on the terminal carbon atom allows them to behave as ligands in coordination compounds[26]. The insertion reaction is one of the most important reactions in organometallic chemistry and simple molecules, notably CO, which is the best studied example, are known to insert into metal - carbon σ-bonds. The isonitrile insertion reaction has been the subject of a review.[111]

Insertion of Isonitrile into Platinum Carbon σ-Bonds

The insertion of isonitrile into platinum carbon σ-bonds has been studied by Treichel and Hess[148] and others.[148,178] The organoplatinum complexes trans-$[PtXR(PR_3)_2]$ react with isonitriles to give the 1:1 ionic four coordinate compounds trans-$[PtR(CNR)(PR_3)_2]X$. When refluxed in benzene or toluene migration of the organic group to the coordinated isonitrile takes place affording trans-$[PtX\{C(R)=NR\}(PR_3)_2]$ (equation 1).

$$\text{trans}[PtXR(PR_3)_2] \xrightarrow{+CNR} \text{trans}\text{-}[PtR(CNR)(PR_3)_2]X \xrightarrow{\Delta} \text{trans}\text{-}[PtX\{C(R)=NR\}(PR_3)_2] \quad (1)$$

The mechanism proposed for this transformation is shown in Scheme I.[148]

Yamamoto et al[118] on the basis of ^{1}Hn.m.r. examinations of some PPh_3 complexes, proposed that the nitrogen of the inserted fragment is weakly coordinated to the metal centre, making the complex five-coordinate.

Erratum p60⇔61

of halide in the presence of sodium perchlorate (equation 3).

$$\underline{cis}\text{-}[PtCl_2(PEt_3)_2] + CNCH_3 \xrightarrow[-NaCl]{NaClO_4} \underline{trans}\text{-}[PtCl(CNCH_3)(PEt_3)_2]^+(ClO_4) \quad (3)$$

Cyanide platinum (II) complexes have been shown to react with $(Me_3O)BF_4$ cleanly to give methyl-isonitrile complexes.[152] $K_2[Pt(CN)_4]$ and $\underline{cis}[Pt(CN)_2(PMePh_2)_2]$ react to give $[Pt(CNCH_3)_4](BF_4)_2$ and $\underline{cis}[Pt(CNCH_3)_2(PMePh_2)_2]$ respectively.

Complexes with the general formula $[PtX_2(CNR)_2]$ {X = halide, NO_2, CN, R = alkyl[153] or aryl[154]} had been prepared by 1914 and it was recognised that they existed as two major classes: $[Pt(CNR)_4][PtX_4]$ and $\underline{cis}$ and $\underline{trans}$ $[PtX_2(CNR)_2]$. Purple crystals of $[Pt(CNR)_4][PtX_4]$ are prepared from $K_2[PtCl_4]$ and the isonitrile and if solutions of these complexes are refluxed colourless crystals of $\underline{cis}[PtX_2(CNR)_2]$ are produced (equation 4).

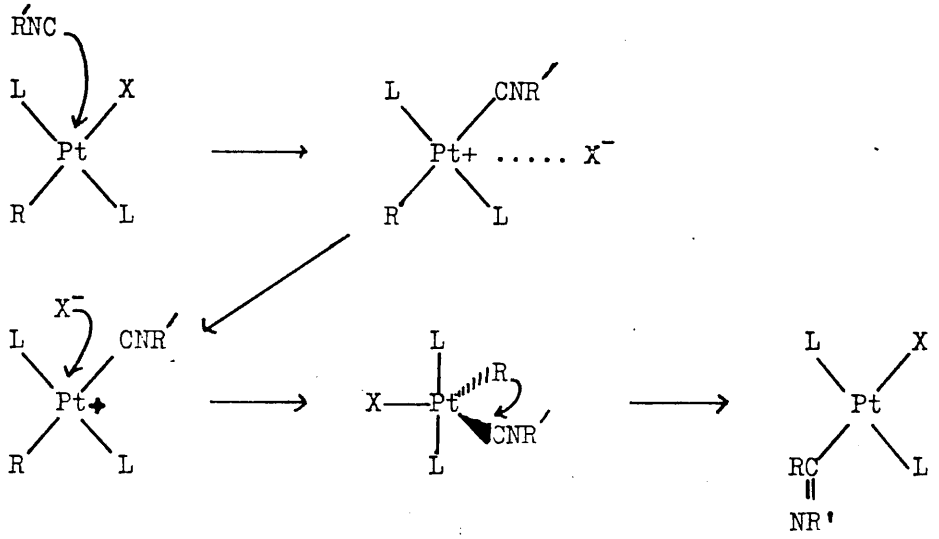
$$K_2[PtCl_4] + 2CNR \longrightarrow \tfrac{1}{2}[Pt(CNR)_4][PtCl_4] \xrightarrow{\Delta} [PtCl_2(CNR)_2] \quad (4)$$

The ligands themselves have penetrating and disgusting odours which are useful for detecting even traces. They have been known since their discovery in the nineteenth century by Gautier[155] and Hofmann[156] independently. The principal synthetic routes include: dehydration of N-monsubstituted formamides RNHCHO;[157] alkylation of a transition metal cyanide ;[155] the 'carbylamine' reaction used originally by Hofmann;[156] deoxygenation of isocyanates or desulphurisation of isothiocyanates;[158] and other methods of a less general applicability.[26]

Bonding in Metal Isonitrile Complexes

The structure of isocyanides can be considered as a hybrid of the

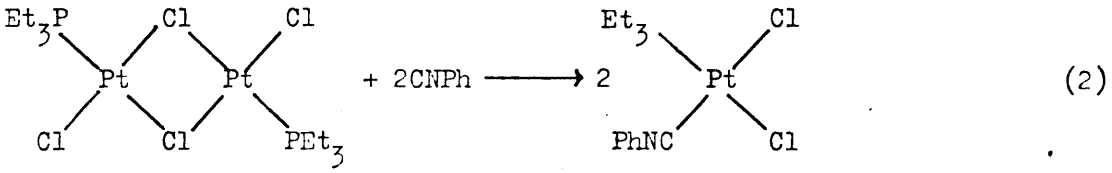
SCHEME I



Platinum Isonitrile Complexes - Preparative Routes

Isonitrile complexes of platinum are more common for the metal in the divalent state[26] although stable zerovalent metal complexes are known.[149] Tetravalent platinum metal complexes may be prepared from the divalent species upon treatment with halogen.

The most widely used preparative route is via cleavage of halide bridge dimer complexes[36,150] (equation 2).



(2)

The colourless crystalline products were shown to be cis from X-ray crystallographic analysis and the stereochemistry of other derivatives is inferred from infrared data.[40]

Ionic four coordinate complexes have been prepared[151] by the displacement

three resonance forms I, II and III as shown:[111]

$$:C{=}N^{-}{-}R^{+} \longleftrightarrow :C{=}N{-}R \longleftrightarrow :C^{-}{=}N^{+}{=}R$$

I II III

Isonitriles as ligands function either as good π-acceptors or as good σ-donors. Discussions of the effect of coordination upon the isocyanide molecule has centred around infrared studies of mixed carbonyl, isonitrile complexes e.g. $[Mn(CNR)(CO)_5]$. The π-accepting ability of CNR in such complexes is lower than that of CO but is generally considered to be slightly better than that of triarylphosphines.[159] In a detailed spectroscopic analysis of Pt, Pd and Ag complexes of methyl isonitrile, Goodfellow et al[160] confirm that CNMe at least, is a poorer π-acceptor than CO, but conclude that it is a much better σ-donor. In PtII isonitrile complexes $\nu(C{\equiv}N)$ is greater than in the free ligand because σ-bonding is more significant in cases such as these.

Results and Discussion

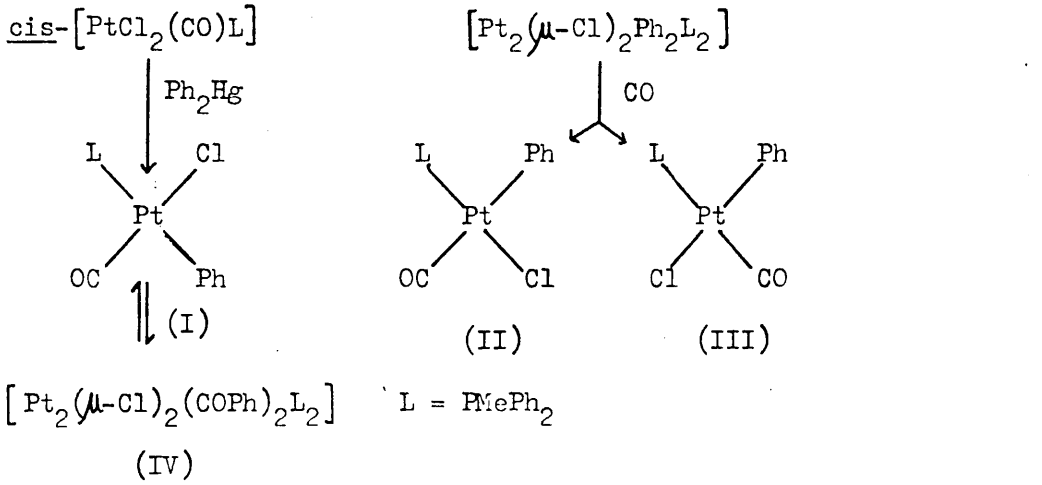
Treatment of the halide bridged dimers $[Pt_2X_4L_2]$ {X is halide; L is tertiary phosphine or arsine} by carbon monoxide gives solutions of the trans isomers of $[PtX_2(CO)L]$[144] some of which can be isolated (equation 5).

$$\begin{matrix} L & & X & & X \\ & Pt & & Pt & \\ X & & X & & L \end{matrix} + 2CO \longrightarrow 2\ \underline{trans}[PtX_2(CO)L] \longrightarrow 2\ \underline{cis}[PtX_2(CO)L] \qquad (5)$$

The trans to cis isomerisation which is spontaneous is also catalysed by free CO, phosphines, or halide ions, and accelerated by light or u.v. irradiation.[144]

The reaction between $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$, which exists in solution as a mixture of trans and cis isomers, and CO, yields a mixture of isomers II and III (Scheme II). At -60°C however, III is predominant from the reaction, and on heating it isomerises to a II/III mixture with more II than III. Attempts to promote insertion in these isomers failed.[51,161]

Scheme II

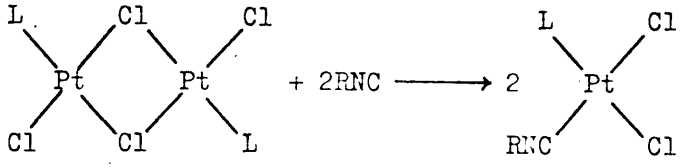


The chloride bridged acyl complexes $[Pt_2(\mu\text{-}Cl)_2(COR)_2(PMePh_2)_2]$ ((I) Scheme II) equilibrate with one isomer of $[PtClR(CO)(PMePh_2)]$ in solution and the equilibrium position is critically dependent on the nature of R. Isomer I is produced initially from the reaction of cis$[PtX_2(CO)L]$ and R_2Hg and only after this step does it equilibrate with IV.[144] Isomers II and III isomerise only very slowly at room temperature to give small amounts of I and IV.[144]

Bridge Cleavage of $[Pt_2X_4L_2]$ by Isonitriles

When benzene suspensions of sym-trans-$[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$ {L = $PMePh_2$, PMe_2Ph, PBu^n_3} are treated with pure methyl isonitrile {L = $PMePh_2$ only} or phenyl isonitrile, pale yellow solutions are obtained from which

the colourless crystalline solids cis-$[PtCl_2(CNR)L]$ may be crysallised (equation 6). These crystals all exhibit terminal isonitrile



(6)

stretching bands in the range 2200-2253cm^{-1}, and show two distinct metal-halide stretching bands, and have $^{31}P\{^1H\}$n.m.r. parameters consistent with a cis stereochemistry (Table 9) as has been established by other workers.[40] Solution infrared spectra of the reactions in $CHCl_3$ or C_6H_6 reveal a single terminal isonitrile stretching band soon after mixing which is the same as that for cis-$[PtCl_2(CNR)L]$.

The major product (90%) after treating a cooled (-60°C) $CDCl_3$ solution of $Et_4N^+[PtCl_3(PMePh_2)]^-$ with 0.6 equivalents of CNPh (as a cooled $CDCl_3$ solution), resonated at δ(P)-10.6 p.p.m. ^1J(P,Pt) 3598Hz, whilst cis-$[PtCl_2(CNPh)(PMePh_2)]$ and 2% of an unknown completed the products. During 100 minutes at this temperature no changes were noted, but after the sample had been maintained at room temperature for 40 minutes the signal for cis-$[PtCl_2(CNPh)(PMePh_2)]$ and the formerly major resonance were present in approximately equal intensity (in total 95%). A solution infrared spectrum (2400-1300cm^{-1}) one hour later at room temperature was the same as an authentic sample of cis-$[PtCl_2(CNPh)(PMePh_2)]$. Since $Et_4N^+[PtCl_3(PMePh_2)]^-$ reacts with CO to give initially trans-$[PtCl_2(CO)(PMePh_2)]$ which then isomerises to the cis isomer, we confidently assign the resonance at δ(P) -10.7 p.p.m. to trans $[PtCl_2(CNPh)(PMePh_2)]$ (Table 9) and the reaction is as in equation 7.

$$Et_4N[PtCl_3(PMePh_2)] + CNPh \xrightarrow[-60^\circ C]{-Et_4N^+Cl^-} \text{trans-}[PtCl_2(CNPh)(PMePh_2)] \xrightarrow{+30^\circ C} \text{cis-}[PtCl_2(CNPh)(PMePh_2)] \quad (7)$$

TABLE 9

Spectroscopic Parameters of cis- and trans-$[PtX_2(CNR)L]$

			cis-$[PtX_2(CNR)L]$			trans-$[PtX_2(CNR)L]$	
L	X	R	$\delta(P)$[a] p.p.m.	$^1J(P,Pt)$/Hz	$\nu(N\equiv C)$[b]/cm^{-1}	$\delta(P)$/p.p.m.	$^1J(P,Pt)$/Hz
PBu^n_3	Cl	Ph	+8.0	3094	2201		
PMe_2Ph	Cl	Ph	-13.6	3143	2208	-22.3[c]	3635
PMe_2Ph	Br	Ph	-13.9	3092	2203	-26.1	3499
$PMePh_2$	Cl	Ph	-1.9	3249	2208	-10.7[c]	3601
$PMePh_2$	Cl	CH_3	-2.7	3276	2235	-9.6	3821
$P(p\text{-tolyl})_3$[d]	Cl	Ph	+6.7	3347	2208		

(a) In $CDCl_3$ relative to 85% H_3PO_4.

(b) For cis isomers, recorded as 0.02 molar solutions in 0.5mm. spacing NaCl window cells.

(c) Recorded at -60°C.

(d) Detected from the reaction of cis $[PtCl_2\{P(p\text{-tolyl})_3\}_2]$, CNPh and S_8, Chapter 3.

The trans/cis isomerisation was no doubt catalysed by $Et_4N^+Cl^-$ (present as a byproduct) in an analogous manner to the CO complexes.[144]

Using a two-jet glass tangential mixing device and capillary, in order to avoid local high concentrations of isonitrile, equimolar 1:1 $CDCl_3/CH_2Cl_2$ solutions of $[Pt_2Cl_4(PMe_2Ph)_2]$ and CNPh were mixed rapidly at -78°C and delivered directly to a 5mm O.D. n.m.r. tube. A $^{31}P-\{^1H\}$n.m.r. spectrum (at -60°C) recorded soon afterwards exhibited signals at δ(P)-22.4 p.p.m. J(P,Pt) 3534Hz for the trans product, and an unknown compound{δ(P)-14.2 p.p.m. ^1J(P,Pt) 2799Hz} in equal intensities (totalling 90% of the product intensity) and another unknown{at δP-17.9 p.p.m. ^1J(P,Pt) unresolved}. Over a period of several hours cis$[PtCl_2(CNPh)(PMe_2Ph)]$ appeared gradually as the other signals decreased in intensity.

The ^1J(P,Pt) of a recently prepared sample of trans-$[PtCl_2(CNBu^t)(PCy_3)]$ is 2842Hz[162] which when compared with our data for the authentic cis$[PtCl_2(CNR)L]$ and the assigned trans isomers is much closer to the value for the cis isomer. This reported parameter is likely to be influenced greatly by the nature of both the bulky PCy_3 and $CNBu^t$ ligands, and these factors alone may account for the discrepancy.

Several experiments on the reaction of isonitriles with dimer were performed before the complications due to inhomogeneous mixing effects were understood. The ^{31}Pn.m.r. spectra recorded for the reactions $[Pt_2X_2L_2]$ {X = Cl, L = $PMePh_2$, PMe_2Ph, X = Br, L = PMe_2Ph} with methyl- (L = $PMePh_2$ only) or phenyl-isonitrile in $CDCl_3$ at room temperature and at -60°C show many phosphine containing products. Typically six

or seven signals for metal bound phosphine were noted initially, of which only a few could be positively identified: cis and trans-$[PtX_2(CNR)L]$, cis and trans-$[PtX_2L_2]$, trans-$[PtX(CNR)L_2]^+$ and $[PtX_3L]^-$. In most cases only cis-$[PtX_2(CNR)L]$ remained after one hour at ambient temperature, but in the reaction of $[Pt_2Cl_4(PMePh_2)_2]$ and MeNC at -60°C $[PtCl_3(PMePh_2)]^-$ and trans-$[PtCl(CNMe)(PMePh_2)_2]^+$ remained in equal amounts after 20 hours at room temperature in the presence of the expected cis product (75%).

Local high concentrations of isonitrile in the vicinity of the likely initial product trans-$[PtX_2(CNR)L]$, resulting in rapid and complicated exchange processes even at -60°C, could give rise to ionic materials of the types identified. Free halide released by these processes could cleave the dimeric reaction constituent to give $[PtX_3L]^-$ (equation 8).

$$[Pt_2X_4L_2] + X^- \longrightarrow [PtX_3L]^- \qquad (8)$$

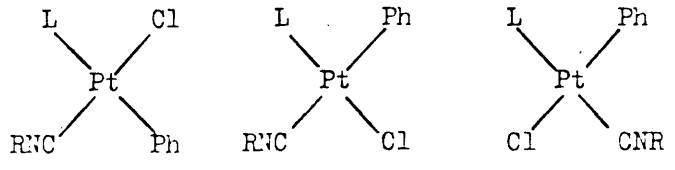
As signals with cis phosphorus-phosphorus two bond coupling constants (typically 20Hz) were not recorded, species such as $[PtXL_3]^+$, cis $[PtX(CNR)L_2]^+$ and $[Pt(CNR)L_3]^{2+}$ could not have been produced in significant concentrations. Finally the appearance of bis-phosphine complexes at all proves the validity of these exchange processes. The observed final product from both the preparative and the spectroscopic experiments cis$[PtX_2(CNR)L_2]$ must therefore be thermodynamic in origin, where CNR was added neat.

The species trans-$[PtCl(CNPh)L_2]^+Cl^-$ {L = $PMePh_2$, PMe_2Ph, PBu^n_3} may be prepared by adding phosphine (L) to cis$[PtCl_2(CNPh)L]$, and their spectroscopic parameters are tabulated in Chapter 3. In the presence of yellow sulphur crystals, solutions of these salts lose phosphine to

give the phosphine sulphides and cis$[PtCl_2(CNPh)L]$ only. The dimer cleavage reactions when repeated in the presence of elemental sulphur failed to show any deviations from that already observed in the absence of S_8. Since neither cis$[PtCl_2(CNPh)L]$ nor isonitrile react with sulphur over periods of several days, and yet trans-$[PtX(CNR)L_2]^+$ is produced in the dimer cleavage experiments, the released phosphine must have reacted more rapidly with some platinum substrate than with sulphur. Mass balance considerations implicate the presence of non-phosphine containing platinum II isonitrile complexes. ^{1}Hn.m.r. spectra of these reactions were too complicated to interpret meaningfully in this respect.

Bridge Cleavage of $[Pt_2(\mu\text{-}Cl)_2Ph_2L_2]$ by Isonitriles

Two equivalents of phenyl-isonitrile and one equivalent of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ {present as cis and trans isomers} react at -78°C (as 1:1 $CDCl_3/CH_2Cl_2$ tangentially mixed solutions) to give two products in near equal amounts. ^{31}Pn.m.r. spectra recorded within a few minutes of mixing show resonances at δ(P) -2.5 p.p.m. ^1J(P,Pt) 4415Hz and δ(P) +5.2 p.p.m. ^1J(P,Pt) 3369Hz. The latter signal has a ^1J(P,Pt) value very close to those values assigned to trans-$[PtCl_2(CNPh)L]$ and accordingly the phosphine in this new complex is trans to CNPh. The remaining resonance has a much higher J^1(P,Pt) value in the range found for phosphines trans to chloride and cis to phenyl, and therefore it is assigned to an isomer II. The latter signal is assigned to an isomer III complex (Scheme III).



I II III

SCHEME III

This reaction differs from the corresponding carbon monoxide experiment in which only an isomer III results from the cleavage of $[Pt_2Cl_2Ph_2(PMePh_2)_2$ at -60°C, but II and III are produced at +30°C.

Deuteriochloroform solutions of cis$[Et_4N][PtCl_2(Ph)(PMePh_2)]$ {prepared in situ by the reaction of $Et_4N^+Cl^-$ and $[Pt_2Cl_2Ph_2(PMePh_2)_2]$} and CNPh react at -60°C to give II and III in yields of 30% and 45% respectively, and a new species with ^{31}Pn.m.r. parameters: δ(P) -1.8 p.p.m. ^1J(P,Pt) 1440Hz (25% yield). The minor constituent has a ^1J(P,Pt) typical of phosphine trans to phenyl and is therefore assigned as isomer I (Scheme III). [This was produced in significant concentrations during the reaction of cis$[PtClPh(PMePh_2)_2]$ and CNPh in the presence of $AgSO_3CF_3$ (Chapter 5). The analogous reaction with CO gave comparable amounts of the well established isomer I -$[PtCl(Ph)(CO)(PMePh_2)]$.]

When this mixture of I, II and III was allowed to come to room temperature and then cooled to -60°C, a ^{31}Pn.m.r. spectrum showed II and III unchanged, whilst I had disappeared to be replaced by a new resonance at δ(P) -5.7 p.p.m. (J^1(P,Pt) unresolved). Isomer I species of the type $[PtClR(CO)PMePh_2)]$ {R = o-tolyl, phenyl, p-MeO_2C-C_6H_4, p-NC-C_6H_4} react rapidly with $Et_4N^+Cl^-$ at room temperature to give the complexes cis $Et_4N^+[PtCl_2(COR)(PMePh_2)]$ identified from their characteristic acyl-carbonyl stretching bands in the region 1611-1615cm^{-1}. These complexes exhibit large ^1J(P,Pt) of 4884-5106Hz (Table 17, Chapter 5) and the phosphorus shifts all lie in the range -5.3 p.p.m. to -6.0 p.p.m. Assuming not unreasonably that iminoacyl ligands are somewhat similar to their acyl counterparts in their mode of bonding to PtII, it is more than coincidental that a CNPh isomer I in the presence of $Et_4N^+Cl^-$

(the byproduct of halide displacement here) disappears upon brief heating to room temperature. The new signal that has appeared in its stead is likely to be due to cis$[Et_4N]^+[PtCl_2\{C(Ph) = NPh\}(PMePh_2)]^-$ (Scheme IV Cation not shown for convenience).

In contrast isomer III is the only product formed from the reaction of CO and cis$[Et_4N]^+[PtCl_2(Ph)(PMePh_2)]^-$ at -60°C in $CDCl_3$, and mixtures of carbonyl II and III only give low concentrations of I after prolonged periods. However, the same trend of insertion is apparent from the isonitrile work, i.e. only I inserts.

Using these assignments other similar complexes of the general formula $[PtCl(R')(CNR)L]$ of isomer I, II and III configurations, were tentatively assigned from similar experiments and their spectroscopic parameters are given in Table 10.

Once again inhomogeneity of mixing conditions has affected the product distribution resultant when neat methyl or phenyl-isonitrile was added to $CDCl_3$ solutions of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ at room temperature or -60°C. As well as II and III species such as trans-$[PtClPh(PMePh_2)_2]$ and trans-$[PtPh(CNR)(PMePh_2)_2]^+$, and in the case of $CNCH_3$ a possible isomer I, were noted. Solutions of trans-$[PtPh(CNR)(PMePh_2)_2]^+Cl^-$ $\{R = Me,Ph\}$ are obtained when CNR is added to trans-$[PtClPh(PMePh_2)_2]$ at room temperature, and when clear solutions such as these are treated with $AgSO_3CF_3$ (or $AgPF_6$) near stoichiometric amounts of a photosensitive precipitate (presumably AgCl) are obtained. The ^{31}Pn.m.r. spectra of these solutions before and after treatment with the silver salt are identical (Table 10) indicating that the halide salts were present (equation 9). Crystalline samples of these complexes were not obtained,

SCHEME IV

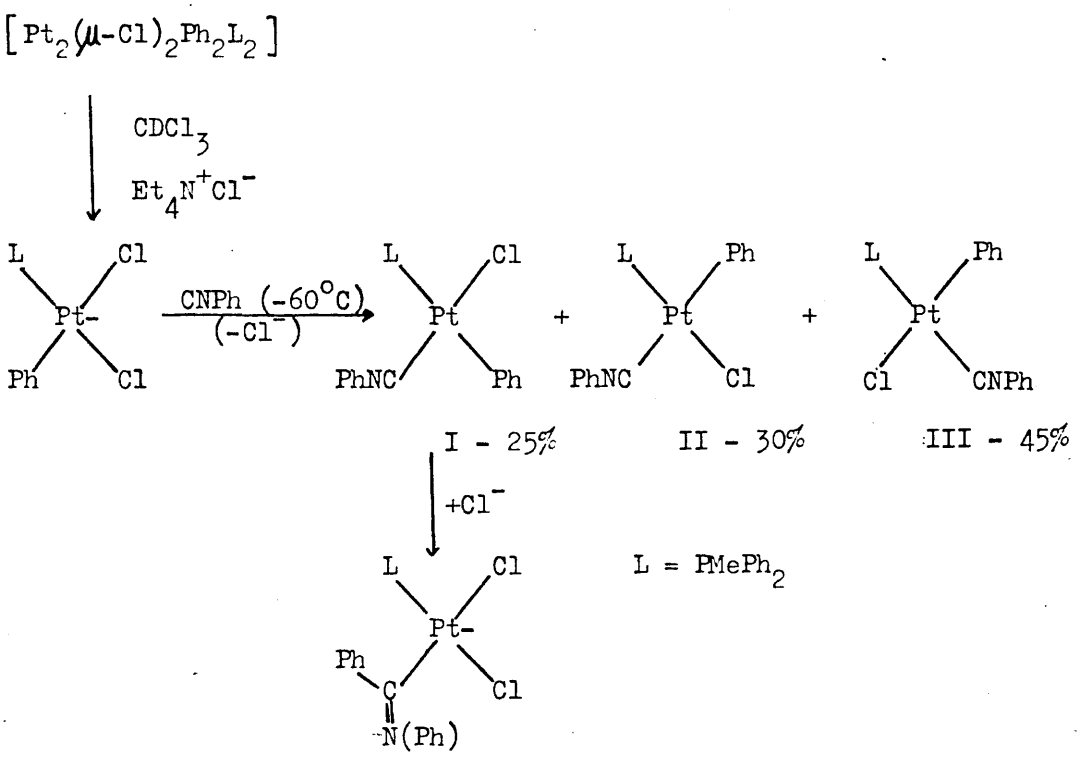

[Pt2(μ-Cl)2Ph2L2]
CDCl3
Et4N+Cl−
CNPh (-60°C)
(-Cl−)
I - 25%
II - 30%
III - 45%
+Cl−
L = PMePh2

TABLE 10

^{31}Pn.m.r. Parameters of $PtClR(CNR')L$ [a]

Complex R	Complex R'	L	Isomer	$\delta(P)$ [b] /p.p.m.	$^1J(P,Pt)$/Hz
Ph	CH_3	$PMePh_2$	I	-1.4	1442
Ph	Ph	$PMePh_2$	I	-1.9	1435
Ph	CH_3	$PMePh_2$	II	-1.7	4195
Ph	Ph	$PMePh_2$	II[c]	-2.7	4404
o-tolyl	CH_3	$PMePh_2$	II	-2.0	4229
CH_3	CH_3	$PMePh_2$	II	+1.6	4205
Ph	CH_3	$PMePh_2$	III[c]	+4.6	3410
Ph	Ph	$PMePh_2$	III[c]	+5.2	3366
Ph	Ph	PMe_2Ph	III	-19.0	3341

(a) I = P *trans* to R, II = P *trans* to Cl, III = P *trans* to CNR'.

(b) As $CDCl_3$ solutions relative to 85% H_3PO_4.

(c) Recorded at -60°C.

TABLE 11

Spectroscopic Parameters of trans-$[PtPh(CNR)(PMePh_2)_2]Cl$ or SO_3CF_3

R	$\delta(P)$[a]/p.p.m.	$^1J(P,Pt)$/Hz	$\delta(H)$[b]/p.p.m.	$^3J(H,Pt)$/Hz	$"J"$[c]$(H,P)"$/Hz	$\nu(N\equiv C)$[d]/cm^{-1}
CH_3	+3.9	2623	[e] 1.66 (6)	35.4	7.9	2248
			[f] 2.88 (3)	11.0	-	
			7.0 - 7.6(20)	-	-	
Ph	+4.0	2655	[e] 1.70 (6)	36.1	7.5	2088
			6.9 - 7.9(25)	-	-	

(a) In $CDCl_3$ at +30°C relative to 85% H_3PO_4.

(b) In $CDCl_3$ relative to TMS; integrals in parenthesis.

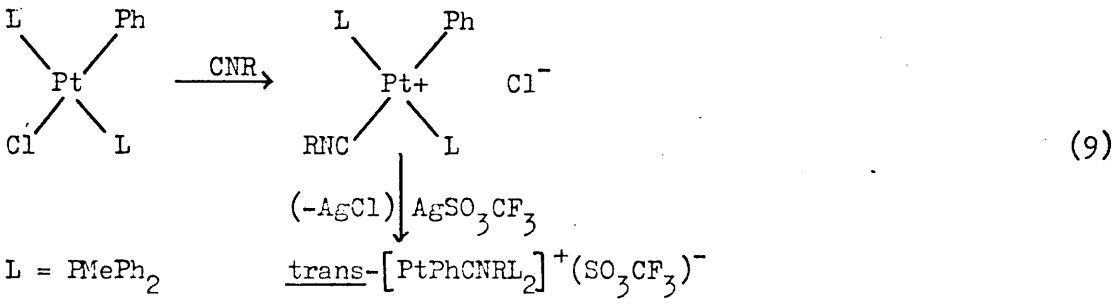
(c) This is $|^2J(H,P) + {}^4J(H,P)|$.

(d) 0.02 molar $CHCl_3$ solutions in 0.5mm spacing NaCl window solution cells.

(e) Phosphine methyl resonance.

(f) Isonitrile methyl resonance.

therefore they were characterised spectroscopically, giving data



(9)

L = $PMePh_2$ $\quad$ <u>trans</u>-$[PtPhCNRL_2]^+(SO_3CF_3)^-$

comparable to known examples.[148]

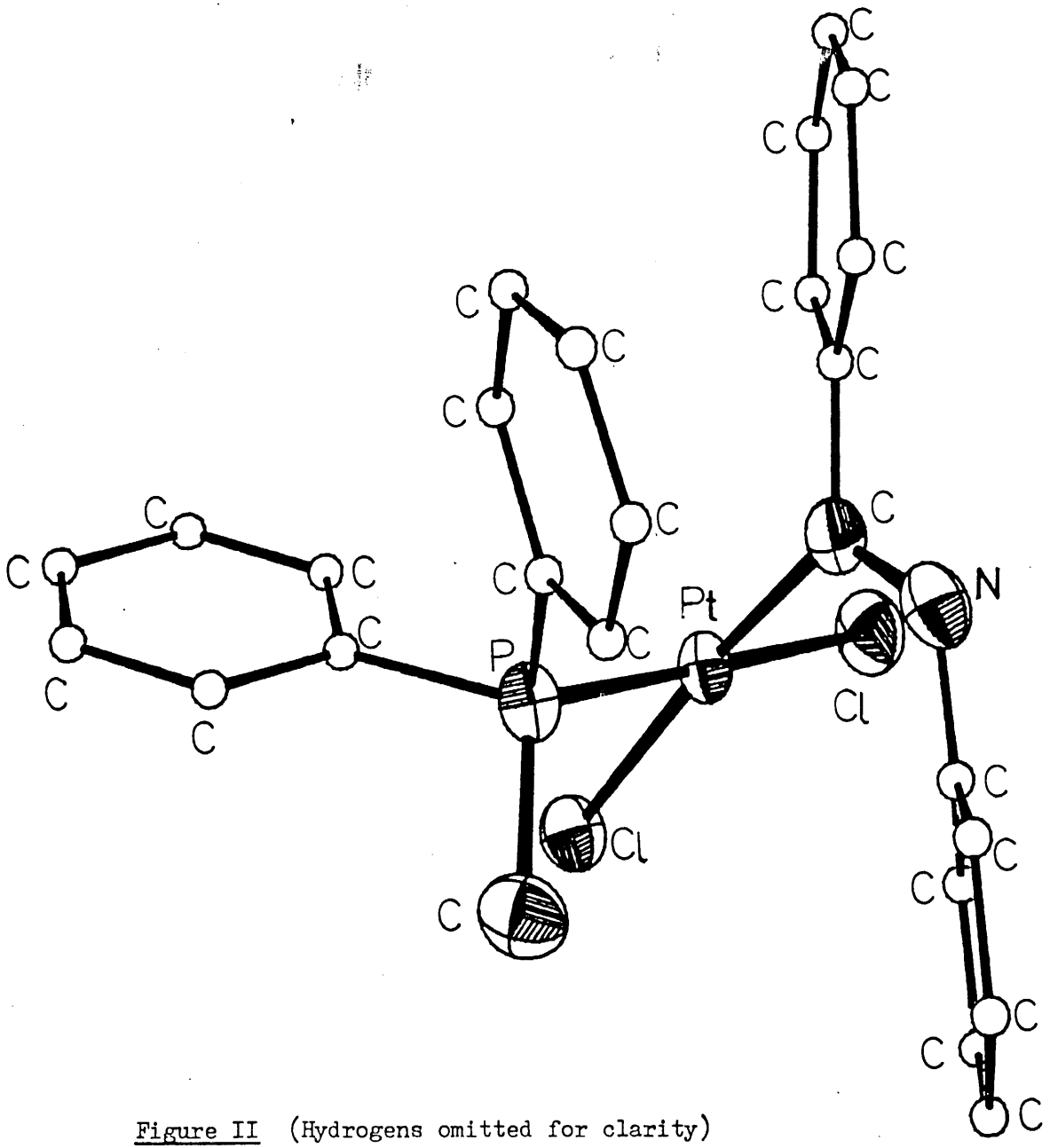
The major phosphine containing product from the reaction of $[Pt_2Cl_2Ph_2(PMePh_2)_2]$ with two equivalents of $CNCH_3$ ca 20 hours after mixing at room temperature (or -60°C) is <u>trans</u>-$[PtPh(CNCH_3)(PMePh_2)_2]^+$ in 90% yield. Amongst the remaining phosphine products were isomers I, II and III and <u>trans</u>$[PtClPh(PMePh_2)_2]$. Higher concentrations of isomer I (20%) persisted for two hours when mixed at -60°C before decreasing in intensity.

Mixing CNPh (2 equivalents) and $[Pt_2Cl_2Ph_2(PMePh_2)_2]$ in $CDCl_3$ also produced a diverse range of products and amongst them was an unusual dimeric platinum complex with asymmetrically substituted terminal sites {δ(P) -3.2 p.p.m. ^1J(P,Pt) 3970Hz ^3J(P,Pt) 45Hz broad, δ(P) -6.2 p.p.m. ^1J(P,Pt) 5045Hz ^3J(P,Pt) 41Hz sharp, same peak integration}. Signals for an analogous species were recorded during the methyl isonitrile reactions.

That same unusual product and some of its analogues are observed in the reactions of <u>cis</u>$[PtCl_2(CNR)L]$ {L = $PMePh_2$, R = Me, Ph} with R'_2Hg {R' = Ph all complexes, R' = Me, <u>o</u>-tolyl, for the $CNCH_3$ derivatives} in $CHCl_3$ or C_6H_6 at room temperature. The only other products from these reactions were the isomer II complexes and in no case was any

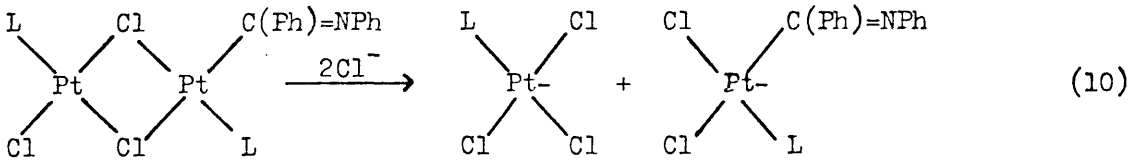
isomer I observed. Repeated attempts at isolating this dimeric constituent chromatographically were unsuccessful (using a 1 metre column of tightly packed silica gel, eluting with ether and ethanol). Eluting the column with ether facilitated total removal of the $PhHgCl$ byproduct in the early fractions, and then ethanol was gradually introduced. Recrystallisation of the poorly separated later fractions yielded small quantities (10-15%) of colourless crystalline cubes only sparingly soluble in $CHCl_3$. A ^{31}Pn.m.r. spectrum of this material (in $(CD_3)_2CO$) exhibited only a single resonance at $\delta(P)$ +5.4 p.p.m. $^1J(P,Pt)$ 3968Hz, which was not observed in the course of the earlier spectroscopic examinations of the reaction of $[PtCl_2(CNR)L]$ and R_2Hg. A KBr infrared spectrum had ν(Pt-Cl) at 284cm^{-1} and 310cm^{-1} and a likely iminoacyl stretch at 1544cm^{-1}. The absolute structure of the complex was confirmed by X-ray crystallographic analysis[162] as the carbene compound cis-$[PtCl_2\{C(Ph)\text{-}N(H)Ph\}(PMePh_2)]$, (Figure II). The reaction of ligated isonitriles with alcohols and amines to form carbenes is well known, and this carbene has effectively been formed by addition of the constituents of benzene! It is more likely however that an iminoacyl moeity has become protonated during the chromatographic treatment.

Despite having failed to isolate this asymmetric dimer it is still possible to deduce structural indications of the terminal ligands from considerations of the $^1J(P,Pt)$ values. The ^{31}Pn.m.r. values are (i) Upfield signal - broad - with $^1J(P,Pt)$ ca 3500-4000 Hz and (ii) Downfield signal - sharp - J(P,Pt) ca 4500-5100Hz. No P-P coupling information. (iii) Two different $^3J(P,Pt)$ values. Benzoyl platinum dimeric complexes $[Pt_2(\mu Cl)_2(COR)_2(PR_3)_2]$ have high $^1J(P,Pt)$ values in the range 5000-5200cm^{-1} as do the complexes cis$[Et_4N][PtCl_2(COR)(PR_3)]$ therefore signal (ii) is assigned to a phosphine cis to an iminoacyl fragment. The remaining


C
C
C

$^1J(P,Pt)$ is in the range of values associated with the tetrahalide complexes $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$, and the monomeric species $[Et_4N][PtCl_3(PMePh_2)]$ The broad nature of the signal could be due to unresolved $^{31}P\text{-}^{14}N$ couplings with an isonitrile nitrogen, but such phenomena are not observed for either cis or trans $[PtX_2(CNR)L]$ (Table 9) or for trans-$[PtX(CNR)L_2]Cl$. There is however a very slight broadening in those signals assigned to isomer III and Anderson et al[162] observed resolved $^1J(^{31}P,^{14}N)$ of 7Hz for $[PtCl_2(CNBu^t)(PCy_3)]$.

When the reaction between cis-$[PtCl_2(CNPh)(PMePh_2)]$ and Ph_2Hg was repeated in the presence of excess $Et_4N^+Cl^-$ (which by itself does not react with the cis complex: ^{1}Hn.m.r. study) large quantities (ca 39%) of $[Et_4N][PtCl_3(PMePh_2)]$ and a resonance at δP -5.7 p.p.m. $^1J(P,Pt)$ 4952 Hz are produced in equal intensities. This latter signal is similar to that observed for cis$[Et_4N][PtCl_2(COPh)(PMePh_2)]$ and is tentatively assigned to the iminoacyl analogue. Furthermore, the two components have probably resulted from the chloride induced bridge cleavage of a dimeric platinum complex with chloride and iminoacyl terminal ligands (equation 10).



(10)

L = $PMePh_2$

The trans configuration is the more likely stereochemistry. Similar results are obtained when excess $Et_4N^+Cl^-$ is added to a solution of the reaction mixture ($[PtCl_2(CNPh)L]$ + Ph_2Hg) after reaction has ceased. The ^{31}Pn.m.r. characteristics of these unusual dimer complexes are given in Table 12.

TABLE 12

^{31}Pn.m.r. Parameters[a] of $[Pt_2(\mu\text{-}Cl)_2Cl(C\{R\}=NR')(PMePh_2)_2]$

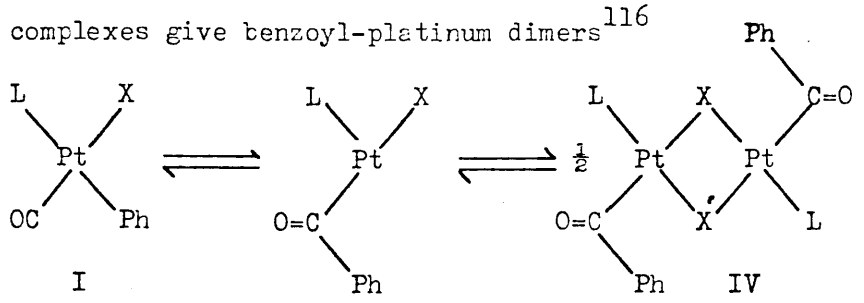
R	R′	δ(P)/p.p.m.[b]	^1J(P,Pt)/Hz	^3J(P,Pt)/Hz
Ph	Ph	-3.2	3969	45 broad
		-6.2	5046	41
o-tolyl	Me	-3.7	3552	(c)broad
		-10.6	4686	
Ph	Me	-3.4	3569	(c)broad
		-9.9	4690	
Me	Me	-3.5	3603	(c)broad
		-10.1	4796	

(a) ^4J(P,P) not resolved.

(b) In $CDCl_3$ at room temperature relative to 85% H_3PO_4.

(c) ^3J(P,Pt) not resolved.

The origin of these unevenly substituted dimeric complexes since they include an iminoacyl terminal ligand, must be intimately related to rate of aryl migration to the isonitrile after the formation of an isomer I, and the mode of dimerisation, which in the instance of CO complexes give benzoyl-platinum dimers[116] (equation 11)



(11)

L = tertiary phosphine, X = halide

During the reaction of cis$[PtCl_2(CNR)L]$ with R_2Hg, if the arylation step is slow relative to the insertion, the resultant 14-electron intermediate formed rapidly from an isomer I in low concentration would have to dimerise with some other PtII complex. In view of the identity of the terminal ligands of the unusual dimeric complexes, it has dimerised with a cis-$[PtCl_2(CNPh)L]$ molecule and lost isonitrile. The displaced isonitrile, from a mass balance viewpoint, has been incorporated in an isonitrile organo-platinum-chloro complex. Such non phosphine containing species must be present in view of the many bis-phosphine platinum complexes produced in these reactions.

Solution infrared spectra of the reactions of cis$[PtCl_2(CNR)L]$ with R'_2Hg in dried $CHCl_3$ show only a gradually broadening and diminishing terminal isonitrile band in the range 2200-2265cm^{-1}. Those reactions involving CH_3NC complexes are over in 1-2 days, whilst the phenyl-isonitrile derivatives continued to react for 9 or 10 days.

Platinum Isonitrile Complexes

For many of the arylation and bridge cleavage reactions of platinum(II) complexes with either bound or free isonitriles, many phosphine complexes are noted which contain higher ratios of phosphine to platinum than were originally present. Many examples are observed in the reaction of neat CNR with the halide bridge dimers $[Pt_2Cl_4L_2]$ and $[Pt_2Cl_2Ph_2L_2]$, of phosphine PtII species which do not contain isonitrile. Not only does this observation prove that complicated exchange processes have occurred but it also suggests that isonitrile organo-platinum-chloride complexes have gone undetected. At this stage it was prudent to investigate the preparation and stability of some isonitrile platinum complexes.

The complexes $[PtCl_2(1,5\text{-cod})]$ and $[PtClPh(1,5\text{-cod})]$ {cod = cyclooctadiene} react in $CHCl_3$ solution with two equivalents of alkyl or aryl isonitrile {methyl, cyclohexyl or phenyl} to give the complexes cis-$[PtCl_2(CNR)_2]$ {Me and Ph} and trans-$[PtClPh(CNR)_2]$ respectively. Cis-$[PtCl_2(CNR)_2]$ are colourless crystalline solids which exhibit two terminal isonitrile stretching bands and two metal chloride stretching bands, which both confirm their cis-stereochemistry. Table 13 lists these spectroscopic parameters. A ^{1}Hn.m.r. spectrum in $CDCl_3$ of the $CNCH_3$ complex shows a sharp triplet at δ(H) 3.64 p.p.m. and ^1J(H,Pt) 18.4Hz. Spectroscopic data for the $CNCH_3$ complex are the same as those observed by Goodfellow et al.[160] $[PtCl_2(CNPh)_2]$ may also be prepared from $K_2[PtCl_4]$ and CNPh via the purple salt $[Pt(CNPh)_4][PtCl_4]$ which rearranges upon refluxing in $CHCl_3$.

Attempts to prepare $[Pt_2(\mu\text{-}Cl)_2Cl_2(CNPh)_2]$ either by refluxing cis$[PtCl_2(CNPh)_2]$ with $[PtCl_2]$ in sym-$C_2H_2Cl_4$, or with $[PtCl_2(NCPh)_2]$ or

TABLE 13

ν(N≡C) and ν(Pt-Cl) of PtII Isonitrile Complexes

Complex	ν(N≡C)/$^{(a)}$cm^{-1}	ν(Pt-Cl/$^{(b)}$cm^{-1}
cis-$[PtCl_2(CNMe)_2]$	2280s, 2258s	325m, 343m
cis-$[PtCl_2(CNPh)_2]$	2240s, 2210s	342m, 348m
trans-$[PtCl_2(CNPh)_2]$		
trans-$[PtCl(Ph_3(CNMe)_2]$	2240s	387m
trans-$[PtClPh(CNCy)_2]$	2250s	300m
trans-$[PtClPh(CNPh)_2]$	2195s	-
$[PtPh(CNMe)_3]SO_3CF_3$	2265s, 2275s, 2302w	-
$[PtPh(CNPh)_3]SO_3CF_3$	2229s, 2212ms, 2258shm	-
$[PtPh(CNCy)_3]SO_3CF_3$	2188s, 2210(sh)ms	-

(a) Recorded as 0.02 molar solutions (in chromophore) in 0.5mm spacing NaCl solution cels. s = strong, m = medium intensity, w = weak, sh = shoulder.

(b) Recorded as KBr discs.

$[PtCl_2(NCMe)_2]$ gave only unreacted and isomerised starting material and decomposition products.

The complexes trans$[PtClPh(CNR)_2]$ {R = Me, Cy or Ph} all exhibit a single intense ν(N≡C) in the range 2200-2260cm^{-1} and single ν(M-Cl) in the region 280-290cm^{-1}. Crystalline material was obtained for the $CNCH_3$ derivative whilst oily solids were produced by the other complexes. In particular the CNPh complex decomposed in chloroform solution over a period of several days producing a brown tarry-oil and some finely divided black solid presumably $[PtCl_2]$ or Pt^{o}. Column chromatographic treatment of this mixture resulted in clear to yellow fractions which behaved in a similar fashion. KBr infrared spectra of these tars indicated the CNPh was lost from the complex and slowly digomerising to give indigo dianils, as does the neat ligand. Crystals of trans-$[PtClPh(CNCy)_2]$ were not obtained; however an infrared spectrum of the colourless oily solid remaining after solvent removal still showed a very intense ν(N≡C) several months later.

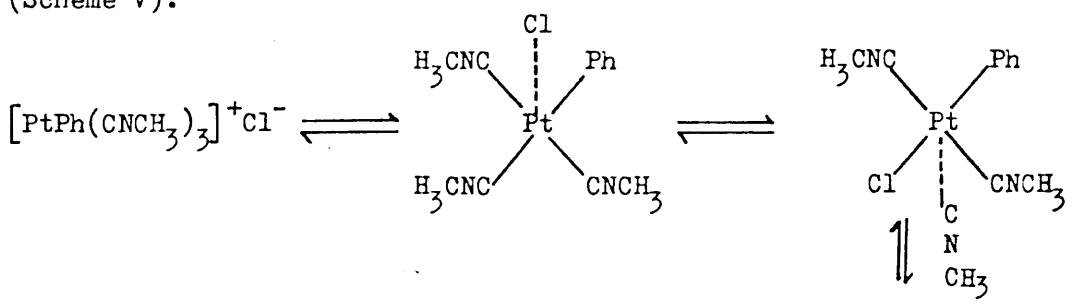
Infrared studies of $[PtCl_2(cod)]$ and $[PtClPh(cod)]$ in the presence of one equivalent of CNR {R = Me,Ph} show the same bands (only weaker) as those of $[PtCl_2(CNR)_2]$ and trans-$[PtClPh(CNR)_2]$ respectively. Presumably subsequent substitution at the initial product (probably an olefin-isonitrile complex) is more favourable than the initial displacement.

Trans-$[PtClPh(CNR)_2]$ as chloroform solutions react with one more equivalent of CNR {R = Me,Ph,Cy} causing a marked change in the C≡N absorption bands at room temperature: a yellow waxy solid in the case of R = Me, and brown and colourless oils for R = Ph or Cy respectively. The CH_3NC

complex gave colourless solutions while as a solid it exuded the smell of isonitrile. Infrared spectra of samples of this solid heated to +60°C under vacuum (ca 0.5 torr) for varying lengths of time (½-5 hours) showed that the complex decomposed by loss of $CNCH_3$ to trans-$[PtClPh(CNCH_3)_2]$ in increasing amounts. Freshly prepared solutions of the yellow complex upon treatment with one equivalent of $AgSO_3CF_3$ yielded a colourless complex whose infrared spectrum differed from that of the yellow solid in only having extra bands for $(SO_3CF_3)^-$. A quantitative amount of AgCl was removed from the mixture indicating that the yellow solid was a chloride salt.

The crystalline solid obtained upon this treatment had a ^{1}Hn.m.r. spectrum which showed a broad uneven triplet at 3.56 p.p.m. with J(Pt-H) ca 17.1Hz and a complicated aromatic peak pattern at 7.2 and 7.3 p.p.m., with integrals 9 and 5 respectively. The spectroscopic and microanalytical data are consistent with the complex $[PtPh(CNCH_3)_3]^+(SO_3CF_3)^-$. Accordingly the yellow solid and the oils obtained in CNPh and CNCy preparations are formulated as $[PtPh(CNR)_3]^+Cl^-$. Attempted preparations of their 'triflate' derivatives were unsuccessful.

^{1}Hn.m.r. spectra of $[PtPh(CNCH_3)_3]^+Cl^-$ (freshly prepared) are identical to the triflate analogue; therefore in view of the stability of the latter to isonitrile loss it must be reasoned that it is chloride reattack on the metal in the solid phase that initiates the displacement (Scheme V).



SCHEME V

trans-$[PtClPh(CNCH_3)_2]$ + $CNCH_3$

Infrared spectra of chloroform solutions (2400-1300cm^{-1}) of the complexes trans$[PtClPh(CHR)_2]$ and $[PtPh(CNR)_3]^+Cl^-$ do not change over periods of several hours when refluxing (except for slight loss of $CNCH_3$ and some polymerisation of CNPh). This indiates the thermal stability of these complexes and their reluctance to undergo insertion, which would have given rise to absorptions in the range 1550-1630cm^{-1}. Treating trans-$[PtClPh(CNR)_2]$ with CO in the presence and in the absence of $AgSO_3CF_3$ gave only very weak metal carbonyl stretching bands which did not increase significantly in intensity once formed. A slight broadening in the isonitrile stretches was apparent however, indicating that mixed isonitrile/carbonyl platinum complexes have only formed in low concentration.

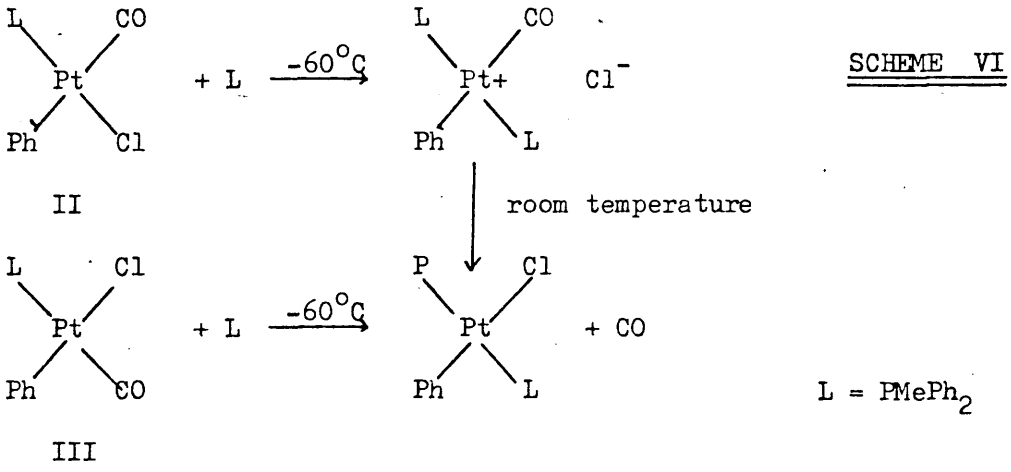
Conclusion

Having now demonstrated the ease of preparation and thermal stability of some organoplatinum (II) isonitrile complexes, it will be noted that they can in many instances account for the apparently unusual stoichiometry of the phosphine containing products in the dimer cleavage reactions. For example the occurrence of trans-$[PtClPh(PMePh_2)_2]$ and trans-$[PtPh(CNR)(PMePh_2)_2]^+$ in the cleavage reactions of $[Pt_2Cl_2Ph_2(PMePh_2)_2]$ by CNR strongly implicate the production of trans-$[PtClPh(CNR)_2]$and other organo-Pt complexes, some of which may be dimeric.

Tangentially mixed solutions of $[Pt_2Cl_2Ph_2(PMePh_2)_2]$ and CNPh react to give II and III at -60°C whereas poorly mixed cis$[Et_4N][PtCl_2(Ph)(PMePh_2)]$ and CNR give I, II and III at the same temperature. It seems reasonable to presume that II and/or III react with CNR to give I, which at -60°C does not insert, but in the presence of halide inserts to give

cis-$[Et_4N][PtCl_2(C\{Ph\}=NPh)(PMePh_2)]$. To produce an isomer I, CNR has displaced phosphine which by reassociating with the metal ends up trans to the phenyl ligand {in the aryl dimer and in isomers II and III L and Ph are cis to one another}. In this way it is possible to account for the appearance of the unusual asymmetric dimer appearing in the dimer cleavage reactions as a result of inhomogeneous mixing. In this reaction the constituents of CNR andPh have been lost from PtII and these may either have been lost separately or as an iminoacyl fragment.

Addition of $PMePh_2$ to a $CDCl_3$ solution of $[PtCl(Ph)(CO)(PMePh_2)]$ isomers II and III at -60°C results in a quantitative reaction of each isomer: III by CO replacement to trans-$[PtClPh(PMePh_2)_2]$, II to the ionic complex trans-$[Pt(Ph)(CO)(PMePh_2)_2]Cl$ (Scheme VI).[51] The analogous isonitrile



SCHEME VI

isomers II and III probably react with displaced $PMePh_2$ to give trans-$[Pt(Ph)(CNR)L_2]^+$ and trans$[PtClPh(PMePh_2)]$ respectively. The isonitrile displaced in forming the latter component could either react with that complex or with any aryl dimer in the vicinity, for it is in poorly mixed aryl dimer cleavage experiments that these materials are observed. Similar arguments centred around the side-reactions of tertiary phosphine, displaced by local excesses of added isonitrile, with the primary product

trans$[PtCl_2(CNR)L]$ in the CNR cleavage of $[Pt_2Cl_4L_2]$ can be applied in order to rationalise the appearance of many bis-phosphine Pt species.

There are close similarities in the bridge cleavage reactions of isonitrile and carbon monoxide, which is unsurprising when one consideres that they are isoelectronic molecules. The two ligands do differ however in their insertion products from $[PtX(Ph)(Y)L]$ isomer I $\{Y = CO, CNR\}$, which for the carbonyls give only benzoyl platinum dimers, but for the isonitrile compounds results in the uncommon asymmetric dimers. Finally, care has to be exercised in interpreting the mechanism of dimer cleavage reactions from the product distributions if there exists any possibility of the process being critically sensitive to the mixing conditions.

Experimental

Infrared spectra of solid samples as KBr discs were recorded on a Perkin Elmer 580 spectrometer. Solution infrared spectra were recorded on a Perkin Elmer 577 instrument, using 0.5mm NaCl solution cells. ^{1}Hn.m.r. spectra were recorded in $CDCl_3$ solution using a Perkin Elmer R32 spectrometer (90MHz) and $^{31}P-\{^1H\}$n.m.r. spectra were obtained from a Varian X.L.100 instrument operating in the Fourier Transform mode.

Methyl and Phenyl-isonitriles were prepared according to procedures A and B respectively of I.K.Ugi et al.[163] All preparation and manupulations with isonitriles were carried out in a fume hood.

Preparation of cis Dichloro(methylisonitrile)(Methyldiphenylphosphino) platinum

Two equivalents of CH_3CN (45 ls, 0.8 moles) were added to a stirred

benzene suspension of sym-trans-$[Pt_2Cl_4(PMePh_2)_2]$ (0.36gms 0.39m moles) to give a bright yellow solution. On standing the solution became paler in colour as a white solid precipitated. Recrystallisation of this solid from CH_2Cl_2/ether gave 0.34gms colourless crystals of cis-$[PtCl_2(CNMe)(PMePh_2)]$, m.pt 206-207°C (decom.) (89% yield). A ^{1}Hn.m.r. spectrum of these crystals in $CDCl_3$ showed the following: δ(H)phosphine 2.4p.p.m. $^2J(H,P)$ 12Hz $^3J(H,Pt)$ 36Hz triplet of doublets; δ(H)isonitrile 2.8p.p.m. $^4J(H,Pt)$ 20Hz broad triplet. Aromatics at 7.5-7.8p.p.m. Relative peak areas 3:3:10 respectively. (Found C36.0, H3.49, N2.75. Calculated for $C_{15}H_{15}Cl_2NPPt$: C35.57, H2.96, N2.77%.

The following were prepared similarly except for cis-$[PtCl_2(CNPh)(PBu^n_3)]$ (with no white precipitate from benzene). This necessitated recrystallisation of the benzene solution residue from CH_2Cl_2/ether.

Cis-dichloro(phenylisonitrile)(methyldiphenylphosphino)(platinum):

m.pt 245-246°C. Found C42.75, H3.06, N2.91. Calculated for $C_{20}H_{18}Cl_2NPPt$, C42.17, H3.16, N2.46%.

Cis-dichloro(phenylisonitrile)(dimethylphenylphosphino)platinum:

m.pt 189-191°C. Found C35.89, H3.11, N2.51%. Calculated for $C_{15}H_{16}Cl_2NPPt$, C35.50, H3.16, N2.76%.

Cis- dichloro(phenylisonitrile)(tri-n-butylphosphino)platinum:

m.pt 122-123°C. Found C39.25, H5.57, N2.23%. Calculated for $C_{19}H_{32}Cl_2NPPt$, C39.92, H5.60, N2.45%.

The Reaction of cis-$[PtCl_2(CNPh)(PMePh_2)]$ and Ph_2Hg

Ph_2Hg (0.2gms 0.56m.moles) was added to a clear 0.02 molar $CHCl_3$ solution of cis$[PtCl_2(CNPh)(PMePh_2)]$ (0.34gms 0.6m.moles) with stirring, to produce

a pale yellow solution. During 8 days at room temperature periodic solution infrared spectra (2400-1300cm^{-1}) showed the originally intense ν(N≡C) of the cis-reactant decay slowly, leaving a weak and broad ν(N≡C) in its place, 2108cm^{-1}. PhHgCl (36mgs) was removed by filtration and the filtrate reduced to dryness to give 0.572gms of an oily residue. Dissolved in a minimum amount of $CHCl_3$ the residue was applied to the top of a 1 metre tightly packed silica gel column (freshly activated) and then eluted with ether (150ml fractions).

After the third and fourth fractions were collected (they contained only small amounts of material) the eluant was gradually replaced by ether/ethanol mixtures, with increasing portions of the latter. After collecting 12 fractions, all the original sample had been collected. Fractions 1-5 contained PhHgCl (confirmed by infrared spectrum and its comparison with that of an authentic sample). Fractions 6-9 contained small amounts of the unseparated mixture (^{31}Pn.m.r. evidence). A ^{31}Pn.m.r. spectrum of the pale yellow-colourless cubic crystals obtained upon crystallisation of fractions 10-12 showed a single component $\{\delta(P)$ -5.4p.p.m. $^1J(P,Pt)$ 3968Hz$\}$ which had not been detected in the unseparated reaction mixture. X-ray crystallographic analysis identified them as cis$[PtCl_2(C\{Ph\}=NHPh)(PMePh_2)]$ - (0.06gms): M.pt.285-286°C. (Found C47,46, H3.79, N1.66, Cl10.08%. Calculated for $C_{26}H_{24}Cl_2NPPt$ C48.22, H3.71, N2.16, Cl10.97%.)

Preparation of Dichloro(1,5-cyclooctadiene)platinum

1,5-Cyclooctadiene (1.3mls 10.2 m moles) was added to a refluxing ethanol suspension of $[PtCl_2]$ (2.0 gms 7.5m moles). Three days later the mixture was cooled and filtered to remove unreacted $[PtCl_2]$ which was washed with

ethanol. The filtrate residue was recrystalissed from CH_2Cl_2/n-pentane and gave 1.83gms of a white powder, whose infrared spectrum (as a KBr disc) was identical to that of an authentic sample of $[PtCl_2(cod)]$ prepared as in reference.[151] Yield 65%.

Preparation of Chlorophenyl (1,5-cyclooctadiene)platinum

To $[PtCl_2(1,5\text{-cod})]$ (2.4gms 6.4m moles) dissolved in 150mls of $CHCl_3$ was added Ph_2Hg (2.0gms, 7.5m moles) with stirring. After stirring for ca 20 hours 1.6gms of PhHgCl as silvery plates was removed by filtration. A further quantity of PhHgCl was obtained when the volume of the solution was reduced. The residue was crystallised from CH_2Cl_2 to give $[PtClPh(cod)]$ (2.45gms 92%).

Cis-Dichlorobis(methylisonitrile)platinum

CH_3NC (40μls 0.4m moles) was added by microlitre syringe to a stirred 0.02 molar $CHCl_3$ solution of $[PtCl_2(1,5\text{-cod})]$ (0.13gms 0.35m moles) in a 50ml r.b. flask. The cooled solution after several hours yielded colourless needles of cis-$[PtCl_2(CNCH_3)_2]$ (0.11gms 95% yield).

The ^{1}Hn.m.r. (90MHz) spectrum in $CDCl_3$ of these crystals and the infrared spectrum as a KBr disc (4000-200cm^{-1}) are identical to those obtained by Goodfellow et al.[160]

cis-Dichlorobis(phenylisonitrile)platinum

Similar to the preparation of $[PtCl_2(CNCH_3)_2]$ above except that ether was added to precipitate colourless crystals of $[PtCl_2(CNPh)_2]$. Yellow crystals

which exhibited a single intense ν(N≡C) were obtained from the mother liquors. These crystals are trans$[PtCl_2(CNPh)_2]$. Found C34.96, H2.28, N5.37%. Calculated for $C_{14}H_{10}Cl_2N_2Pt$. C35.58, H2.12, H5.93%.

Preparation of cis$[PtCl_2(CNPh)_2]$ from K_2PtCl_4

PhNC (1ml, 9.5m. moles) was added with stirring to an aqueous solution of K_2PtCl_4 (2gm, 4.82m moles). The solution colour deepened from a pink to a deep purple almost immediately and after a few minutes a finely divided purple precipitate of $[Pt(CNPh)_4][PtCl_4]$ developed, which was removed by filtration and washed with water and ether (1.98gms 87%).

All of this salt suspended in $CHCl_3$ was refluxed for four hours to produce a pale brown solution. After filtration, ether was added to the filtrate and a creamy precipitate was obtained.

Attempted Preparation of Di(μ-chloro)dichlorobis(isocyanophenyl) diplatinum

When $[PtCl_2(CNPh)_2]$ and $[PtCl_2]$ are refluxed overnight in sym-tetrachloroethane the two reactants are recovered cleanly from the mixture. Similarly cis$[PtCl_2(CNPh)_2]$ and $[PtCl_2(PhCN)_2]$ may be recovered virtually unreacted after a similar treatment in $CHCl_3$.

A mixture of cis-$[PtCl_2(CNPh)_2]$ (0.5gms, 1.1m moles) and $[PtCl_2(CH_3CN)_2]$ (0.33gms, 0.95m moles) in 100mls of $CHCl_3$ maintained under a nitrogen atmosphere were refluxed for a total of 3 hours. After 75 minutes an infrared spectrum of this solution (2400-1300cm^{-1}) showed a single terminal isonitrile band at 2214cm^{-1}, where before there were two ν(N≡C).

After refluxing, the now pale brown reaction mixture was filtered and the solvent was removed to yield 0.55gms of a sand-yellow solid, whose infrared spectrum (KBr disc) showed only a single broad ν(N≡C) at 2210cm^{-1}. An infrared spectrum of the solid precipitate (0.27gms) removed by filtration showed it to consist largely of $[PtCl_2(CH_3NC)_2]$ after comparison with an authentic sample.

Repeated attempts at crystallising this material from $CHCl_3$, C_6H_6 or ethanol produced ever darkening brown solutions and accompanying black precipitates from decomposition. The single terminal isonitrile stretching band and what may be a single metal halide stretching band at 345cm^{-1} strongly suggest that this solid may be trans-$[PtCl_2(CNPh)_2]$ (no microanalysis). Over long periods of time (2-3 weeks) solutions of cis$[PtCl_2(CNPh)_2]$ decomposed similarly.

Attempted preparations of trans$[PtClPh(CNR)_2]$ {R = Cy,Ph} and $[PtPh(CNPh_3)]^+(Cl^-$ or $SO_3CF_3)$ gave either colourless oils (R = Cy) or brown tarry oils (R = Ph) which could not be crystallised.

Preparation of trans-Chlorophenylbis(methylisonitrile)platinum

CH_3NC (51 ls 0.96m moles) was added with stirring to a 0.02 molar $CHCl_3$ solution of $[PtClPh(1,5\text{-cod})]$ (0.20gm 0.48m moles) and the reaction was monitored by recording solution infrared spectra (2400-1300cm^{-1}) periodically. Soon after adding the isonitrile a very intense ν(N≡C)str at 2230cm^{-1} with shoulders a 2244cm^{-1} (intense) and 2250cm^{-1}(very weak) had appeared. Thirty minutes later the solvent was removed and the residue was crystallised from ethanol to yield colourless needles of trans-$[PtClPh(CNCH_3)_2]$ (0.18gms 98% yield). (Calculated for $C_{10}H_{11}ClN_2Pt$,

C30.80, H2.82, C18.11 and N7.19%. Found C30.66, H2.75, C19.3 and N7.07%.) The crystals did not melt below 320°C although at 180°C they began to darken in normal and polarised light.

Preparation of Phenyltris(methylisonitrile)platinumtrifluoromethanesulphonate

CH_3NC (70µls 1.3m moles) was added to a 0.02 molar $CHCl_3$ solution of $[PtClPh(cod)]$ (0.16gms 0.39m moles) in which was suspended $AgSO_3CF_3$ (0.10gms 0.39m moles). After 30 minutes the mixture was filtered to give 0.05gms of a darkening solid (AgCl). The filtrate residue was crystallised from CH_2Cl_2 ether to give colourless needles of $[PtPh(CNCH_3)_3]SO_3CF_3$ (0.2gms 95%) mpt 180-181°C. (Calculated for $C_{13}H_{14}F_3N_3O_3PtS$. C28.67, H2.57, N7.72%. Found C28.75, H2.45, H7.62%.) $[PtPh(CNCH_3)_3]SO_3CF_3$ may also be prepared from $[PtClPh(CNCH_3)_2]$ $AgSO_3CF_3$ and $CNCH_3$.

CHAPTER FIVE

THE REACTIONS OF $[PtX(Ph)(PR'_3)_2]$

WITH CARBON MONOXIDE AND ISONITRILES

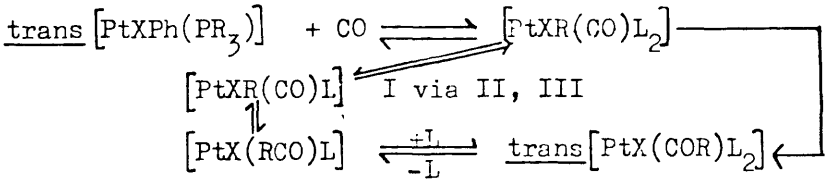
Chapter 5 - Introduction

The insertion reaction is thought to be an intermediate step in many organic syntheses that are catalysed by transition metal complexes and it is an important aspect of the Ziegler Natta catalysed polymerisation of olefins. Mechanistic studies[165,166] of carbonyl insertion across a platinum-alkyl bond (or alkyl migration from metal to carbon monoxide) have highlighted some features of reactivity which differ markedly from those observed for substitution reactions at platinum (II). The mechanism of isonitrile insertion at platinum is less well understood but a study[167] of carbonyl- and isonitrile-insertion in the same molecule show strong similarities.

Results and Discussion

Trans-$[PtX(Ph)(PR_3)_2]$ reacts with carbon monoxide to produce[51] by phosphine loss isomers II and III of the general formula $[PtXPh(CO)(PR_3)]$ {II: PR_3 trans to X, III: PR_3 trans to CO}, which convert to the remaining isomer with Ph trans to PR_3. Migration then proceeds to form a benzoyl intermediate (Scheme I) which then reacts with PR_3 to give

SCHEME I



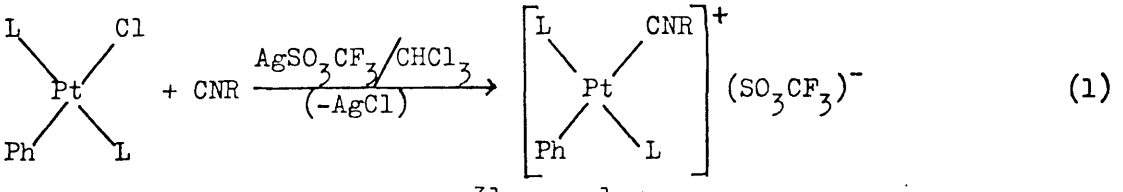
the expected trans-$[PtX(COPh)(PR_3)_2]$.[51] A direct carbonyl insertion route via a five-coordinate intermediate also operates independently of the phosphine elimination pathways, and this becomes the predominant pathway with more nucleophilic PR_3. Elemental sulphur, when used to 'trap' the PR_3 as their phosphine sulphides, was instrumental in

identifying some intermediates.[51] A detailed kinetic investigation[168] of the insertion of CO into trans-$[PtXR(PR_3)]$ to produce trans $[PtX(COR)(PR_3)_2]$ has been carried out by Heck and co-workers.[168]

Investigations of the reactions of trans$[PtXR(PPh_3)_2]$ with methyl-isonitrile have been performed by Treichel and co-workers.[148] They noted the initial formation of the 1:1 electrolytes trans-$[PtR(CNMe)(PPh_3)_2]^+Cl^-$. When solutions of these salts were refluxed for a suitable length of time they were converted cleanly into the iminoacyl complexes trans-$[PtX\{C(R)=NMe\}(PPh_3)_2]$.[148] The mechanism proposed by these workers favoured aryl or alkyl migration at a five-coordinate intermediate with apical phosphines, formed as a consequence of attack by the halide X^- at the cation centre. (See Chapter 4)

The Reactions of trans-$[PtClPh(PMePh_2)_2]$ with $CNCH_3$ and CNPh

Phenyl- and methyl-isonitriles react with chloroform solutions of trans-$[PtClPh(PMePh_2)_2]$ in the presence of excess $AgSO_3CF_3$ to give the salts trans-$[PtPh(CNR)(PMePh_2)_2]\,SO_3CF_3$ as oily solids (equation 1).



(1)

The salts exhibit distinctive ^{31}P and ^1Hn.m.r. characteristics (approximately same shift $\delta(P)$ +4.0 p.p.m. and coupling parameters $^1J(P,Pt)$ 2630Hz as well as virtually coupled phosphine methyl protons) and sharp $\nu(N\equiv C)$. Attempts to crystallise the oils, from a wide variety of solvents, were unsuccessful. Whilst the chloride analogue of the $CNCH_3$ derivative is unchanged in chloroform solution after 40 days at ambient temperature, the phenyl-isonitrile variant behaves in a more

complicated manner.

Immediately after adding half an equivalent of CNPh to trans-$[PtClPh(PMePh_2)_2]$ in $CDCl_3$ at room temperature, the salt trans-$[PtPh(CNPh)(PMePh_2)_2]^+Cl^-$ formed as expected, but only as 75% of the products. Half an equivalent of trans$[PtClPh(PMePh_2)_2]$ remained in excess, and took no further part in the reaction. The remaining 25% of the products was an unknown bis-phosphine platinum complex exhibiting a cis-phosphorus-phosphorus two bond coupling constant $\{^2J(P,P)cis\}$ of 19.2Hz. The one bond phosphorus-platinum coupling constants $\{^1J(P,Pt)\}$ of its phosphines at 1608 and4411Hz are indicative of two cis-phosphines trans to an organic moeity and a chloride respectively (see Appendix). Two days later the salt formed only 30% of the products whilst the cis- complex represents 50% of the total and a new unknown $\{\delta(P)$ +3.8p.p.m. $^1J(P,Pt)$ 3068Hz$\}$ accounted for the remaining 20%. Solution infrared spectra $(2400\text{-}1300cm^{-1})$ of a 0.02 molar $CHCl_3$ solution of a similar mixture showed a dramatic decrease in the intensity of $\nu(NC)$ after the same period of time. This observation and the close similarity of the $^1J(P,Pt)$'s of this complex and of trans-$[PtClPh(PMePh_2)_2]$ allow us to assign it as the complex trans-$[PtCl\{C(Ph)=NPh\}(PMePh_2)_2]$. After 40 days the proportions of trans-$[PtPh(CNPh)(PMePh_2)_2]^+Cl^-$ cis complex and iminoacyl complex were 26%, 24% and 50% respectively. Decreases in both the salt and the unknown cis complex concentrations are accompanied by increases in the concentration of the iminoacyl product, accordingly the cis-complex is assigned as cis-$[PtCl(C\{Ph\}=NPh)(PMePh_2)_2]$. Reassuringly the $^1J(P,Pt)$ of the phosphine trans to chloride in this complex is similar to that noted in cis$[PtClPh(PMePh_2)_2]$.

The rate of reaction of aliphatic and mixed aliphatic/aromatic tertiary phosphines with sulphur to give the corresponding sulphides is known to be too fast to measure.[147] Whilst carbonylating trans-$[PtX(Ph)(PR_3)_2]$ in the presence of yellow sulphur in excess Anderson and Cross detected isomers II (P trans to Cl) and III (P trans to CO) of $[PtX(Ph)(CO)(PR_3)]$ by 'trapping' the displaced PR_3 as the sulphide. Methyl iodide has been used to 'trap' the phosphine as the phosphonium salt, although less successfully.

When one equivalent of CNPh is added to a $CDCl_3$ solution of trans-$[PtClPh(PMePh_2)_2]$ in the present of excess sulphur (ca 30mol equivalents) at room temperature, a far lower concentration of cis-$[PtCl(C(Ph)=NPh)(PMePh_2)_2]$ is produced (only 8%) and starting material persists despite adding sufficient CNPh. Approximately half as much trans-$[PtPh(CNPh)(PMePh_2)_2]^+Cl^-$ (35%) is noted whilst Ph_2MePS (15%) and isomers III (P trans to CNPh) and I (P trans to Ph) or II (P trans to Cl) in equal amounts (total 12%) account for the remaining products. After 90% reaction the proportions of Ph_2MePS and the salt are 40% and 10% respectively, and all the other products are unchanged. Whilst the sulphide represents 40% of the product after 90 minutes, those phosphine platinum species that have appeared as a result of a single phosphine loss from either the salt or the cis complex account for only one quarter of this. There is clearly more Ph_2MePS {δ(P) +35.9 p.p.m.} than can be explained for by this route and the presence of unreacted starting material is significant in this respect. It seems likely that subsequent displacement of phosphine from III and I (or II) has occurred to give complexes such as $[PtClPh(CNPh)_2]$ or $[PtPh(CNPh)_3]^+Cl^-$, and their survival could possibly be an artifact of the sulphur presence. In

this experiment the lower concentration of the cis-iminoacyl complex suggests that it either loses tertiary phosphine itself or that a phosphine is displaced prior to its generation, which has been trapped as a sulphide. Spectroscopic data for the complexes detected in these reactions are given in Table 14.

The five-coordinate pathway for methyl-isonitrile insertion proposed[148] by Treichel and Hess on the basis of ^{1}Hn.m.r. investigations of the final products and the ionic intermediates (trans-$[PtPh(CNCH_3)(PPh_3)_2]^+I^-$) makes no mention of the possible involvement of cis-bis phosphine intermediates. While insertion by a purely five-coordinate mechanism might be favoured for the Ph_3P complexes as it appears to be during the carbonylation of trans-$[PtClPh(PPh_3)_2]$[51] the reaction of trans-$[PtClPh(PMePh_2)_2]$ and CNPh demonstrates that this is not the only pathway and that a more complicated process may operate alongside it, or instead of it.

No cis-bis-phosphine complexes are detected during the carbonylation of trans-$[PtXPh(PR_3)_2]$ and no isomer I $[PtXPh(CO)(PR_3)]$ (P trans to Ph) is evident in those cases where an equivalent of phosphine is trapped as the sulphide.[51] It is the complexes II and III of that same general formula that are observed, and these isomerise to I before insertion occurs. Independent experiments have shown that II and III do not insert, and attempts to promote insertion led only to CO loss.[51]

The Reactions of $[PtClPhL_2]$ with L $\{L = PMePh_2, PPh_3\}$

When $PMePh_2$ is added as pure liquid to a $CDCl_3$ solution of trans-$[PtClPh(PMePh_2)_2]$ at ambient temperature the ^{1}Hn.m.r. resonances of

TABLE 14

^{31}Pn.m.r. Parameters of Organoplatinum (II) Isonitrile Complexes

{L = $PMePh_2$}

	$\delta(P)$[(a)] /p.p.m.	$^1J(P,Pt)$/Hz
trans-$[PtClPhL_2]$	+8.7	3010
trans-$[PtPh(CNCH_3)L_2]Cl$(or SO_3CF_3)[(b)]	+3.9	2623
trans-$[PtPh(CNPh)L_2]Cl$(or SO_3CF_3)[(c)]	+4.0	2655
cis-$[PtCl(C\{Ph\}=NPh)L_2]$[(d)]	2.1d[(e)]	1608
	-3.2d	4411
trans-$[PtCl(C\{Ph\}=NPh)L_2]$	+3.8	3068
$[PtClPh(CNPh)L]$ {P trans to Ph} I	-1.9	1435
$[PtClPh(CNPh)L]$ {P trans to Cl} II	-2.7	4404
$[PtClPh(CNPh)L]$ {P trans to CNPh} III	+5.2	3366

(a) Relative to 85% H_3PO_4 in $CDCl_3$ at +30°C: positive shifts are downfield.

(b) $\nu(N\equiv C)$ 2262cm^{-1}

(c) $\nu(N\equiv C)$ 2208cm^{-1}

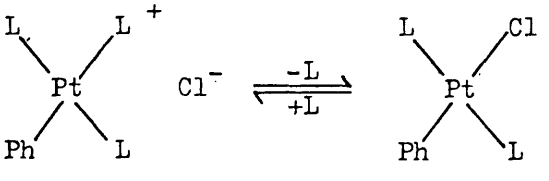
recorded as 0.02 molar $CHCl_3$ solutions in 0.5mm spacing NaCl window cells.

(d) $^2J(P,P)$ is 19.2Hz

(e) d = doublet

the phosphine methyl-protons change from a sharply defined triplet of triplets{δ(H) 1.17 p.p.m. ^3J(H,Pt) 34Hz, $|^2J(H,P)+^4J(H,P)|$ 7Hz} to a poorly resolved broad triplet {δ(H) 1.67 p.p.m. ^3J(H,Pt) ca 33-34Hz}. At -60°C phosphorus 31 n.m.r. spectra of the mixture show sharp signals for $[PtPh(PMePh_2)_3]Cl^-$ and the starting material (88% and 12% respectively). The proportions of salt and trans-$[PtClPh(PMePh_2)_2]$ are 53% and 47% respectively at 0°C and the signals are slightly broadened. After shaking the mixture for 5 minutes with a slight excess of $AgSO_3CF_3$ a ^{31}Pn.m.r. spectrum at ambient temperature showed that the solution consisted entirely of a tris-phosphine salt. The ^{1}Hn.m.r. spectrum of this sample in the range 1.43-1.9 p.p.m. had two overlapping phosphine methyl resonances {virtually coupled trans phosphine methyls δ(H) 1.43 p.p.m. ^3J(H,Pt) 32.8Hz $|^2J(H,P)+^4J(H,P)|$ = 7.9Hz - a triplet of triplets, and δ(H) 1.62 p.p.m. ^2J(H,P) 6Hz, ^3J(H,Pt) ca 26Hz satellites concealed, a triplet of doublets. Relative proportions 2:1}. The ^{31}Pn.m.r. parameters of the 'triflate' (SO_3CF_3) and chloride derivatives of the salt are identical.

The complex $[PtPh(PMePh_2)_3]^+Cl^-$ undergoes rapid ligand exchange at room temperature which, although slower, still operates at -60°C but is halted by removal of chloride from the system (equation 2). The



(2)

L = $PMePh_2$

salt interconverts exclusively with the trans isomer of $[PtClPh(PMePh_2)_2]$. The strong trans influence of the aryl-substituent no doubt makes the phosphine trans to it more labile with respect to displacement by chloride than the other two neutral ligands.

When a cooled (-60°C) $CDCl_3$ solution of $PMePh_2$ is added to a $CDCl_3$ solution of cis $[PtClPh(PMePh_2)_2]$ at -60°C in the presence of excess sulphur, $[PtPh(PMePh_2)_3]^+Cl^-$ is produced and not Ph_2MePS. Clearly the cis complex reacts with phosphine more rapidly than does the sulphur. With the phosphine present as less than one equivalent no isomerisation took place at -60°C during 20 minutes at this temperature and only upon warming to room temperature did isomerisation and phosphine sulphide formation proceed. It would appear that ligand exchange between $[PtPh(PMePh_2)_3]^+Cl^-$ and the cis complex is either very slow, or does not occur. In view of the results of the reaction of trans-$[PtClPh(PMePh_2)_2]$ and $PMePh_2$ the latter conclusion is the more accurate one.

Attempts to prepare $CDCl_3$ solutions of $[PtPh(PPh_3)_3]^+Cl^-$ from trans-$[PtClPh(PPh_3)_2]$ and PPh_3 at room temperature, or from the cis isomer and PPh_3 at -60°C, were unsuccessful despite introducing $AgSO_3CF_3$ to the room temperature experiment. In the room temperature examination of trans-$[PtClPh(PPh_3)_2]$ and PPh_3, signals for the free phosphine and the trans complex only were noted.

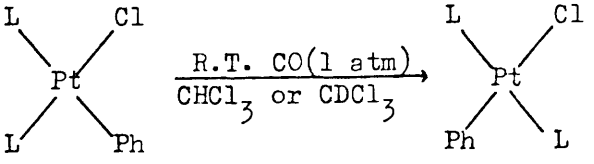
When cis-$[PtClPh(PPh_3)_2]$ and PPh_3 are mixed as $CDCl_3$ solutions at -60°C signals for both the starting materials remained whilst a prominent resonance at δ(P) +22.4 p.p.m. appeared as 40% of the product (no apparent satellites). Surprisingly cis-$[PtCl_2(PPh_3)_2]$ was present as 20% of the products. Two unknown signals in equal proportions {δ(P) +22.8 p.p.m. ^1J(P,Pt) unresolved, δ(P) +28.6 p.p.m. J(P,Pt) 4768Hz in total 40%} were also apparent. After the sample had been left overnight at room temperature the reaction had only proceeded to 40% completion. The

products were trans-$[PtClPh(PPh_3)_2]$ 35%, the singlet resonance at δ(P) +22.4 p.p.m. 33%, an unknown {δ(P) +32.0 p.p.m. ^1J(P.Pt) unresolved} 16% and cis-$[PtCl_2(PPh_3)_2]$ 16%. One week later all the unreacted starting material was trans, PPh_3 was now apparent and the other products were unchanged. Upon repeating this reaction with a higher ratio of phosphine to cis starting material, greater amounts of the species with a signal at δ(P) +22.4 p.p.m. were obtained. However, the absence of any obvious ligand exchange characteristics for this sharp resonance and its connection with the broad free PPh_3 signal at δ(P) ca-7.0 p.p.m. is puzzling. Whilst it is difficult to identify this species it can only be a product of cis-$[PtClPh(PPh_3)_2]$ and PPh_3 and could quite possibly be a neutral five-coordinate species: formula $[PtClPh(PPh_3)_3]$ with three equatorial phosphines.

Romeo et al have reported [169] the preparation of many alkyl-tris-triphenylphosphine platinum ionic complexes, and in their examinations of the reactions of trans$[PtCl(aryl)(PPh_3)_2]$ with PPh_3 they conclude that steric overcrowding prevents the formation of the aryl-derivatives.[169]

The Reactions of cis$[PtClPhL_2]$ {L = $PMePh_2$, PPh_3} with Carbon Monoxide

The reactions of cis-$[PtClPhL_2]$ with carbon monoxide in chloroform solution are essentially very simple at room temperature. Treating the complexes for only ca 2 minutes with CO resulted in almost total isomerisation to the trans isomers (equation 3). In the presence of

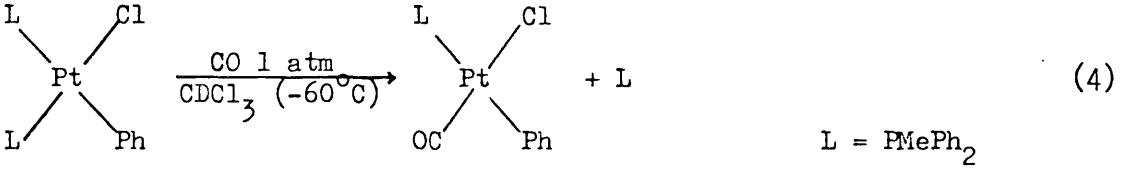


(3)

excess $AgSO_3CF_3$ or $AgPF_6$ substantial amounts of trans-$[PtPh(CO)L_2]^+Y^-$

$\{Y^- = (SO_3CF_3)^-, PF_6^-\}$ were produced. At -60°C however, isomerisation was suppressed sufficiently to allow the varied and complicated carbonylation pathways of the cis compounds to be observed.

Formation of isomer I $[PtClPh(CO)(PMePh_2)]$ (Ph trans to P) proceeds somewhat faster than isomerisation at -60°C in the carbonylation of cis-$[PtClPh(PMePh_2)_2]$ (equation 4). After one hour isomerisation had



(4)

proceeded 10% whilst isomer I formed 40% of the product intensity. The displaced phosphine appears in the product $[PtPh(PMePh_2)_3]^+Cl^-$ regardless of whether the reaction is performed in the presence of excess sulphur or not, therefore it has been formed from the reaction of cis-$[PtClPh(PMePh_2)_2]$ with the phosphine. Trans-$[PtPhCO(PMePh_2)_2]^+Cl^-$ accounts for the remaining 10% of the products. On warming to room temperature trans-$[PtCl(COPh)(PMePh_2)_2]$ appears in place of signals for isomer I and $[PtPh(PMePh_2)_3]^+Cl^-$, which do not survive. The amount of inserted product (only 10%) is less than the concentration of isomer I at -60°C whilst trans-$[PtClPh(PMePh_2)_2]$ forms the remainder of the product.

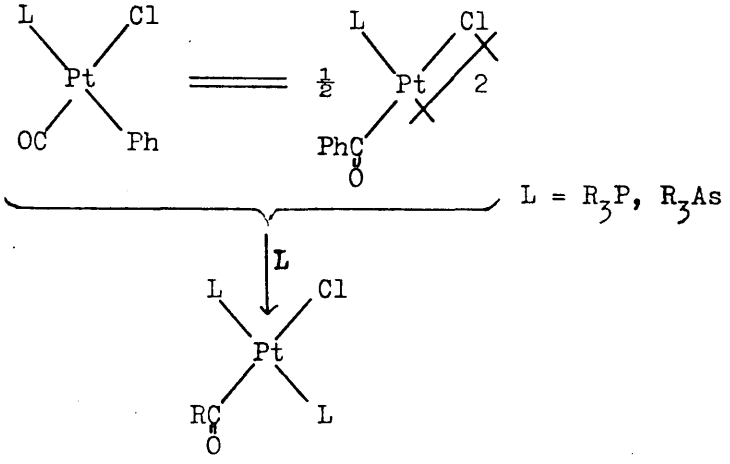
During the carbonylation of cis$[PtClPh(PPh_3)_2]$ at -60°C isomerisation is much reduced with respect to the $PMePh_2$ system, and less isomer I $[PtClPh(CO)(PPh_3)]$ (P trans to Ph) is produced (15%), after a similar period of time. In the presence of yellow sulphur crystals no $SPPh_3$ is noted and no obvious signals for $[PtPhL_3]^+$ (L = PPh_3) species could be identified: typically doublet and triplet resonances with a $^2J(P,P)$ of ca 20Hz. The same sharp singlet singlet resonance at δP +22.4 p.p.m.

observed in the reaction of cis-$[PtClPh(PPh_3)_2]$ and PPh_3 is apparent and it must hold the missing PPh_3. Comparisons of its signal intensity with that of isomer I from several spectra recorded during 90 minutes at -60°C, as the carbonylation reaction proceeded, suggest that the ratio of phosphine to platinum for this unknown is 3:1. After 100 minutes of treatment with CO at -60°C the reaction had attained 70% completion and the products were isomer I $[PtClPhCO(PPh_3)]$ and the complex with $\delta(P)$ +22.4 p.p.m. in equal amounts totalling 75%, trans-$[PtClPh(PPh_3)_2]$ 17% and cis-$[PtCl_2(PPh_3)_2]$ 8%.

Upon warming this mixture to room temperature all the remaining cis-$[PtClPh(PPh_3)_2]$ isomerises, whilst the isomer I and the unknown $\{\delta(P)$ +22.4$\}$ disappear, to be replaced by trans-$[PtCl(COPh)(PPh_3)_2]$ (18%). Trans-$[PtClPh(PPh_3)_2]$ now represents 73% of the total signal intensity and cis-$[PtCl_2(PPh_3)_2]$ and an unknown $\{\delta(P)$ -1.4 p.p.m. $^1J(P,Pt)$ unresolved$\}$ account for 5% and 4% respectively.

In both the PPh_3 and $PMePh_2$ sets of carbonylation reactions multivarious processes ensue upon warming the complex reaction mixtures to ambient temperature from -60°C. These include: (i) isomerisation of unreacted cis-$[PtClPhL_2]$ perhaps by the excess CO in the system without incorporation of CO: (ii) decarbonylation of trans-$[PtPh(CO)L_2]^+$ $\{L = PPh_3, PMePh_2\}$ to give trans-$[PtClPhL_2]$: (iii) ligand exchange by $[PtPh(PMePh_2)_3]^+Cl^-$ and its PPh_3 equivalent to give trans-$[PtClPhL_2]$ and phosphine: (iv) carbonyl insertion to give trans-$[PtCl(COPh)L_2]$ either from the isomer I and the displaced tertiary phosphine, or possibly from a portion of the unreacted cis-$[PtClPhL_2]$ and dissolved CO.

One striking aspect of these reactions is the absence of any insertion at -60°C despite the availability of displaced phosphine and potentially inserting isomer I species. It has been reported[116] that monomeric benzoyl complexes are formed from the reaction of isomer I/benzoyl platinum dimer mixtures with tertiary phosphine or arsine at room temperature, regardless of the position of the equilibrium.[116] (Equation 5)



(5)

When $[PtClPh(CO)(PMePh_2)]$ (Ph trans to P) is prepared from Ph_2Hg and cis $[PtCl_2(CO)(PMePh_2)]$ in $CDCl_3$ at low temperature (ca -30°C) aryl migration and consequent benzoyl dimer equilibration only proceeds at elevated temperatures.[116] Such halide bridged benzoyl platinum dimers are not observed during the carbonylation of cis-$[PtClPhL_2]$ (L = $PMePh_2$, PPh_3) at -60°C, nor are they detected upon warming the reaction mixtures to room temperature, and the final concentrations of inserted product (trans-$[PtCl(COPh)L_2]$) at room temperature are always less than the amounts of isomer I complex present prior to warming. Obviously there is a secondary process operating in the reaction of isomer I with tertiary phosphine, that involves CO loss.

The Reactions of Isomer I Complexes with R_3P, Cl^- and CO

A knowledge of the reactions by which the isomer I complexes are lost

upon warming the carbonylation mixtures to ambient temperatures is vital if this problem surrounding insertion is to be understood. The products of the reactions of the isomer I species with carbon monoxide, tertiary phosphine and chloride might provide an insight into the pathways to both insertion and CO loss.

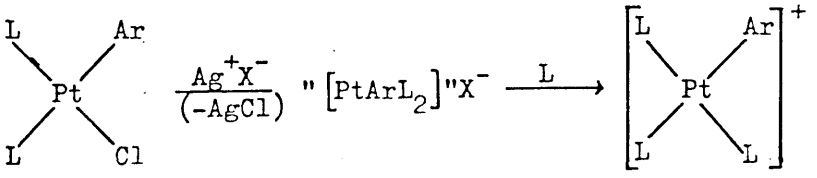
The isomer I complexes $[PtCl(pNC\text{-}C_6H_4)(CO)(PPh_3)]$ and $[PtCl(\underline{o}\text{-}MeO\text{-}C_6H_4)(CO)(PMePh_2)]$ (in each case $Y\text{-}C_6H_4$ is trans to P) react with PPh_3 and $PMePh_2$ respectively in deuteriochloroform solution at room temperature to give trans-$[PtCl(Y\text{-}C_6H_4)L_2]$ (Y = pNC-, L = PPh_3; Y = oMeO, L = $PMePh_2$) as the only product. These particular functional groups on the aryl ligand inhibit spontaneous insertion electronically (pNC) and sterically (o-MeO) at ambient temperatures and thus allow the reactions of isomer I to be studied without the complication of side reactions with an aryl-dimer.

The major product from the reaction of $[PtCl(\underline{o}MeO\text{-}C_6H_4)(CO)(PMePh_2)]$ {δ(P) +7.1 p.p.m. ^1J(P,Pt) 1534Hz} and $PMePh_2$ at -60°C (mixed tangentially as equimolar $CDCl_3$; CH_2Cl_2 (1:1) solutions) is $[PtCl(\underline{o}\text{-}MeO\text{-}C_6H_4)(PMePh_2)_2]$ (cis:trans 7.5:1) 42% which at this temperature maintains its isomeric ratio despite the presence of displaced CO. The salt $[Pt(\underline{o}MeO\text{-}C_6H_4)(PMePh_2)_3]^+Cl^-$ accounts for 33% of the total products, and 17% appears as trans-$[Pt(\underline{o}\text{-}MeO\text{-}C_6H_4)(CO)(PMePh_2)_2]^+Cl^-$ {δ(P) +3.8p.p.m. ^1J(P,Pt) 2462Hz}. The remaining 8% of the products consists of cis-$[PtCl_2(PMePh_2)_2]$ and an unknown {δ(P) -2.3p.p.m. ^1J(P,Pt) unresolved} in equal amounts. Significantly, despite adding one full equivalent of $PMePh_2$, some isomer I remains in approximately the same concentration as there is $[Pt(\underline{o}\text{-}MeO\text{-}C_6H_4)(PMePh_2)_3]^+Cl^-$. It is almost certainly the case that incoming phosphine has reacted as rapidly with cis-$[PtCl(\underline{o}\text{-}MeO\text{-}C_6H_4)(PMePh_2)_2]$ (the product of the reaction of isomer I with

$PMePh_2$) as it does with isomer I. It is unlikely that such concentrations of isomer I and $[Pt(\underline{o}MeO\text{-}C_6H_4)(PMePh_2)_3]^+Cl^-$ could have resulted from the reaction if $\underline{cis}\text{-}[PtCl(\underline{o}MeO\text{-}C_6H_4)(PMePh_2)_2]$ and displaced CO since they generally necessitate prolonged treatment of the cis complex with CO at -60°C.

Upon warming this reaction mixture to room temperature all the $[PtCl(\underline{o}MeO\text{-}C_6H_4)(PMePh_2)_2]$ becomes trans (47%) and apart from ca 5% $\underline{cis}[PtCl_2(PMePh_2)_2]$ the only other product (48%) has the parameters $\delta(P)$ +5.8p.p.m. $^1J(P,Pt)$ 3276Hz. A solution infrared spectrum of this mixture (2400-1200cm^{-1}) revealed a moderately intense $\nu(CO)$acyl at 1610cm^{-1}, and no terminal carbonyl stretching modes. The acyl-stretching band, and the similarity of the unknown's n.m.r. parameters with those of $\underline{trans}\text{-}[PtCl(COPh)(PMePh_2)_2]$ $\{\delta(P)$ +5.2 p.p.m. $^1J(P,Pt)$ 3211Hz$\}$ allow us to assign this product as $\underline{trans}\text{-}[PtCl(\underline{o}MeO\text{-}C_6H_4\text{-}CO)(PMePh_2)_2]$.

If the reaction of $[PtCl(\underline{o}MeO\text{-}C_6H_4)(CO)(PMePh_2)]$ (P trans to Ph) and $PMePh_2$ is repeated in the presence of $AgCO_3CF_3$ at -60°C in $CDCl_3$ (the silver salt does not affect isomer I by itself) increased amounts of $[Pt(\underline{o}\text{-}MeO\text{-}C_6H_4)(PMePh_2)]^+$ appear, whilst the same quantity of $[Pt(\underline{o}MeO\text{-}C_6H_4)(CO)(PMePh_2)_2]^+$ is produced. $[PtCl(\underline{o}\text{-}MeO\text{-}C_6H_4)(PMePh_2)_2]$ represents only 11% of the product and less cis- isomer is produced (2:1 cis: trans). Obviously the reaction of $\underline{cis}[PtCl(\underline{o}MeO\text{-}C_6H_4)(PMePh_2)_2]$ with the incoming phosphine is favoured by the removal of halide from the tris-phosphine complex when it is formed reversibly, or by removal of ligated halide from the cis complex (equation 6). Unknown species



(6)

Ar = $\underline{o}MeO\text{-}C_6H_4$ X = SO_3CF_3 L = $PMePh_2$

{δ(P) +0.9 p.p.m. ^{1}J(P,Pt) 1765Hz 15%, δ(P) +0.4 p.p.m. ^{1}J(P,Pt) 3248Hz 4%} and cis-$[PtCl_2(PMePh_2)_2]$ (5%) are also noted. On warming the mixture to room temperature trans-$[PtCl(CO\text{-}C_6H_4\text{-}oMeO)(PMePh_2)_2]$ appears as 9% of the product whilst the concentrations of the tris-phosphine ionic complex and trans-$[Pt(oMeO\text{-}C_6H_4)(CO)(PMePh_2)_3]^+(SO_3CF_3)^-$ increase to 61% and 19% respectively. Only 5% of the products are represented as trans-$[PtCl(oMeO\text{-}C_6H_4)(PMePh_2)_2]$, isomer I accounts for 2% and the unknown at δP +0.9 p.p.m. ^{1}J(P,Pt) 1765Hz remains as 4% of the final mixture.

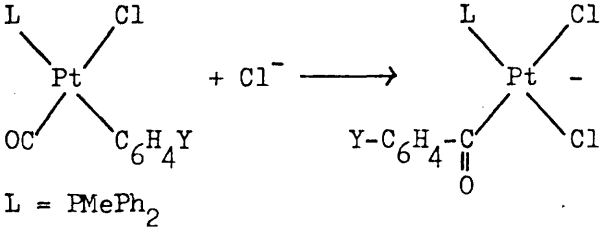
Apparently insertion in both of these experiments has arisen from the complex interreactions of dissolved CO, cis-$[PtCl(oMeO\text{-}C_6H_4)(PMePh_2)_2]$, possibly isomer I and certainly tertiary phosphine which is displaced from the tris phosphine complex upon warming.

Large quantities of the decomposition product cis-$[PtCl_2(Ph_3P)_2]$ {δ(P) +14.4 ^{1}J(P,Pt) 3679Hz}, 20% are apparent soon after mixing $[PtCl(pNC\text{-}C_6H_4)(CO)(PPh_3)]$ (P trans to pNC-C_6H_4) {δ(P) +18.3 p.p.m. ^{1}J(P,Pt) 1617Hz} and PPh_3 in $CDCl_3$ at -60°C. The major product is cis-$[PtCl(pNC\text{-}C_6H_4)(PPh_3)_2]$ 68%, whilst an unknown tris phosphine complex {δ(P)s +23.6 p.p.m. d and 12.0 p.p.m. t, ^{2}J(P,P) 18.8Hz ^{1}J(P,Pt)s unresolved} (5%), trans-$[Pt(pNC\text{-}C_6H_4)(CO)(PPh_3)_2]^+Cl^-$ {δ(P) 31.8 p.p.m. ^{1}J(P,Pt) 2660Hz} (3%) and isomer I (4%) complete the list of products. When the sample is allowed to warm to room temperature the total concentration of $[PtCl(pNC\text{-}C_6H_4)(PPh_3)_2]$ (72%) changes little except that now the isomer ratio is 9:5 trans:cis. The other products are cis-$[PtCl_2(PPh_3)_2]$ (23%), trans-$[Pt(pNC\text{-}C_6H_4)(CO)(PPh_3)_2]^+Cl^-$ (3%) and an unknown {δ(P) +28.7 p.p.m. ^{1}J(P,Pt) unresolved} 2%. There are no

products from insertion, and the reaction has given products similar to the room temperature run except for the decomposition that has occurred.

Ph_3P reacts with a 1:1 isomer I $[PtClPh(CO)(PPh_3)]$ (Ph trans to P)/ $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PPh_3)_2]$ mixture to give trans-$[PtCl(COPh)(PPh_3)_2]$ as 60% and $[PtClPh(PPh_3)_2]$ as 40% (cis:trans ratio ca 1:1) of the total product signal intensity at -60°C. Soon after warming the mixture to room temperature the ratio of trans-$[PtClPh(PPh_3)_2]$ with respct to cis was ca 2:1 (35%) whilst the inserted product increased slightly in concentration to ca 65%.

At room temperature the isomer I complexes $[PtCl(Y\text{-}C_6H_4)(CO)(PMePh_2)]$ (Y = o-Me, p-NC, pH , pCO_2Me) react with excess $Et_4N^+Cl^-$ to give the complexes Et_4N^+ cis-$[PtCl_2(COC_6H_4\text{-}Y)(PMePh_2)]^-$ ν(CO) acyl 1603cm^{-1} → 1614cm^{-1} δ(P) -5.3 → -6.0 p.p.m. ^1J(P,Pt) 4900-5000Hz, Table 2 . (Equation 7.)



(7)

L = $PMePh_2$

Although free chloride might be available at -60°C in the form of $[PtRL_3]^+Cl^-$ (or its PPh_3) equivalent) insertion by this means does not prevail at -60°C: in fact there is no insertion at all at -60°C from the carbonylation of cis-$[PtClPhL_2]$ (L = PPh_3 or $PMePh_2$). Upon warming the carbonylation product mixtures from -60°C to +30°C this type of inserted product should appear in accord with those reactions of isomer I and Cl^- at room temperature. However the concentration of free halide would be severely limited by its attack on $[PtPhL_3]^+$

to give the trans-$[PtClPhL_2]$ which also becomes prevalent at higher temperatures. Accordingly insertion by this pathway does not occur during the carbonylation of cis-$[PtClPhL_2]$ ($L = PPh_3$ or $PMePh_2$) at $-60^{\circ}C$ or upon warming the reaction mixtures to room temperature.

The complex $[PtCl(pNC\text{-}C_6H_4)(CO)(PMePh_2)]$ (P trans to $pNC\text{-}C_6H_4$) {δ(P) +5.7 p.p.m. ^1J(P,Pt) 1462Hz} in $CHCl_3$ when treated at room temperature with CO for 24 hours remained intact. When this reaction was repeated at $-60^{\circ}C$ in $CDCl_3$ in the presence of excess $AgSO_3CF_3$ the isomer I complex still did not react. Upon warming this isomer I and $AgSO_3CF_3$ to $+30^{\circ}C$ decomposition occurred and of the many products only trans-$[Pt(pNC\text{-}C_6H_4)(CO)(PMePh_2)_2]^+$ could be identified, (ca 10%).

During the reaction of cis-$[PtClPhL_2]$ ($L = PPh_3$, $PMePh_2$) with CO at $-60^{\circ}C$ inserted products do not appear even after 2 hours of treatment, despite the considerable concentrations of the isomer I complexes and a potential source of free phosphine in the guise of $[PtPhL_3]^+Cl^-$ (or its equivalent for $L = PPh_3$). Obviously tertiary phosphine is released too slowly from complexes such as $[PtPh(PMePh_2)_3]^+Cl^-$ at $-60^{\circ}C$ to be of any benefit. More importantly the isomer I complexes react with phosphine at this low temperature, not to give inserted products (trans-$[PtCl(COPh)L_2]$), but via CO displacement to give cis-$[PtClPhL_2]$ and then $[PtPhL_3]^+Cl^-$. When a typical reaction mixture at $-60^{\circ}C$ is warmed to room temperature insertion proceeds to a small extent (ca 10-15% of the products are trans-$[PtCl(COPh)L_2]$). This insertion coincides with the disappearance of $[PtPhL_3]^+Cl^-$ and isomer I, and the isomerisation of the remaining cis-$[PtClPhL_2]$ to the trans form.

The equilibration of $[PtPhL_3]^+Cl^-$ with trans-$[PtClPhL_2]$ and displaced phosphine is more favourable at ambient temperatures (approaching 0^oC). Isomer I and the remaining cis-$[PtClPhL_2]$ react competitively with the displaced phosphine. At lower temperatures isomer I reacts by CO loss to give cis-$[PtClPhL_2]$ but at higher temperatures insertion would occur to give trans-$[PtCl(COPh)L_2]$. The cis-$[PtClPhL_2]$ would react with phosphine to regenerate the ionic trisphosphine complex, and the cycle of reactions would continue as a dynamic equilibrium. The reaction of some of the cis-$[PtClPhL_2]$ with CO would continue to provide isomer I and $[PtPhL_3]^+Cl^-$ to fuel this reaction cycle.

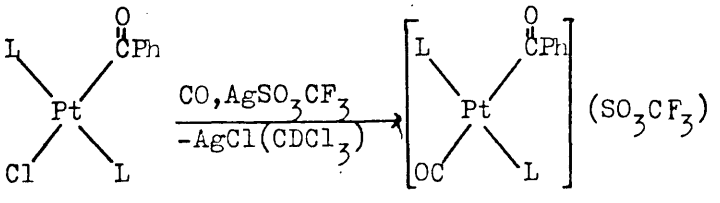
Further work is needed to establish whether a different temperature, between -60^oC and $+30^oC$, would be suitable for improving the yield of inserted product in these carbonylation reactions. An intermediate temperature at which the rate of isomerisation of cis-$[PtClPhL_2]$ was not too rapid in comparison with the other processes which do lead to insertion (i.e. displacement of phosphine (L) from $[PtPhL_3]^+$ by Cl^-, and the reaction of L with isomer I to give trans-$[PtCl(COPh)L_2]$). The reaction of cis-$[PtClPhL_2]$ with CO and the isomerisation process may be the initial steps of a general insertion scheme.

The Influence of Silver Ion on the Carbonylation of cis-$[PtClPhL_2]$

When cis-$[PtClPhL_2]$ (L = $PMePh_2$, PPh_3) are carbonylated in the presence of excess $AgSO_3CF_3$ at -60^oC in $CDCl_3$:ether (ca 10:1) they are exhausted more rapidly than in the presence of excess sulphur (which has no effect): completion in 70-80 minutes for the former reaction as opposed to 53% reaction after 90 minutes in the presence of sulphur.

After 70 minutes at -60°C all the starting material had reacted during the carbonylation of cis-$[PtClPh(PMePh_2)_2]$ leaving only three species. The major products were $[PtPh(PMePh_2)_3]SO_3CF_3$ and $[PtClPh(CO)(PMePh_2)]$ (P trans to Ph, an isomer I) in equal amounts totalling ca 79%, and an unknown cis bis phosphine complex {δ(P) -0.3 p.p.m.d and -4.0 p.p.m.d, $^2J(P,P)$ 24.2Hz and $^1J(P,Pt)$'s 3296 and 1780Hz respectively} represented the remaining 21% of the products. The phosphorus of the unknown which has the smaller $^1J(P,Pt)$ is trans to an organic group, whilst its partner in the complex has a $^1J(P,Pt)$ typical of phosphorus trans to carbon monoxide. Whilst the other two products are the same as those obtained in the absence of silver salt, this new species is particular to this reaction.

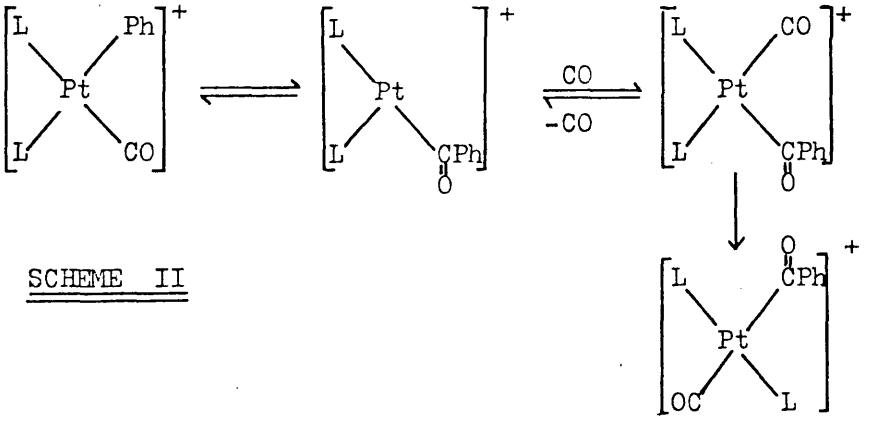
As this mixture was warmed briefly to room temperature and then cooled to -60°C the $[PtPh(PMePh_2)_3]SO_3CF_3$ was now 48% abundant, whilst isomer I decreased greatly in concentration to 6%, and trans-$[PtPh(CO)(PMePh_2)_2]SO_3CF_3$ now appeared as 13% of the products. The remaining 33% of the product range was a new unknown {δ(P) -1.0 p.p.m. $^1J(P,Pt)$ 2782Hz}. In an independent experiment the same resonance is obtained when trans-$[PtCl(COPh)(PMePh_2)_2]$ is treated with CO in the presence of $AgSO_3CF_3$, and it is assigned to the complex trans-$[Pt(COPh)(CO)(PMePh_2)_2]SO_3CF_3$ (equation 8). The carbonylation reaction



(8)

mixture converted totally to trans-$[PtPh(CO)(PMePh_2)_2](SO_3CF_3)$ and trans-$[Pt(COPh)(CO)(PMePh_2)_2](SO_3CF_3)$ 20% and 80% respectively when left overnight at room temperature.

The narrowness of the range of $^{1}J(P,Pt)$ values for phosphurus trans to alkyl or aryl ligands in PtII complexes at ca 1400-1900Hz does not allow us to assign the unknown cis complex obtained at -60°C unambiguously. It could either be the phenyl-complex cis-$[PtPh(CO)(PMePh_2)_2]SO_3CF_3$ or its benzoyl-analogue cis-$[Pt(COPh)(CO)(PMePh_2)_2]SO_3CF_3$. Spontaneous insertion followed by further carbonylation and then isomerisation to give trans-$[Pt(COPh)(CO)(PMePh_2)_2]SO_3CF_3$ might be the fate of the phenyl complex upon warming to +30°C (Scheme II) whilst a benzoyl complex would no doubt isomerise. In view of the lack of inserted products



SCHEME II

in other similar carbonylation reactions at -60°C the first suggestion is probably the correct one, although a novel rapid insertion at -60°C cannot be ruled out. It is only by repeating the experiment with labelled ^{13}CO that an unambiguous assignment could be made, depending upon the extent of extra $J(P-^{13}C)$ values observed.

After treating cis-$[PtClPh(PPh_3)_2]$ with CO in the presence of excess $AgSO_3CF_3$ for one hour at -60°C in $CDCl_3$:ether (5:1) the reaction had proceeded to 90% completion, and 50% of the product consisted of an unknown cis compound similar to that observed for the $PMePh_2$ case, {$\delta(P)$ +19.6 p.p.m.d, +11.7 p.p.m.d, $^{2}J(P,P)$ 21Hz and $^{1}J(P,Pt)$ 3471 and 1666Hz respectively}. The next major product was trans-

$[PtPh(CO)(PPh_3)_2]SO_3CF_3$ (25%) and isomer I $[PtClPh(CO)(PPh_3)]$ (P trans to Ph) and another unknown complex with shift δ(P) +22.4 p.p.m. (containing the displaced PPh_3) were present in comparable amounts (total 20%). The only other species present was trans-$[PtClPh(PPh_3)_2]$ 5%. On warming to room temperature all of the cis materials became trans and a singlet resonance {δ(P) +14.2 p.p.m. J(P,Pt) 2911Hz } represented 60% of the products. The only remaining species was trans-$[PtPh(CO)(PPh_3)_2](SO_3CF_3)$. The unknown major product has ^{31}Pn.m.r. parameters identical to those of trans-$[Pt(COPh)(CO)(PPh_3)_2]$ prepared from the reaction of trans-$[PtCl(COPh)(PPh_3)_2]$ and CO in the presence of $AgSO_3CF_3$ at room temperature.

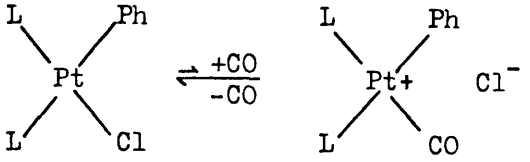
The unknown cis complex noted at -60°C has spectroscopic parameters compatible with either cis-$[PtPh(CO)(PPh_3)_2]SO_3CF_3$ or cis-$[Pt(COPh)(CO)(PPh_3)_2]SO_3CF_3$. For the same reasons as those used in the $PMePh_2$ case, the phenyl complex is the more probable candidate.

Cis-$[PtClPhL_2]$ (L = $PMePh_2$, PPh_3) are made in situ fairly cleanly (ca 95% yield or greater) by the action of ethereal HCl on $CDCl_3$ solutions of cis-$[PtPh_2L_2]$. However, when $[PtPh_2(dpe)]$ (dpe = 1.2 bis(diphenylphosphino) ethane) is treated thus, only 40% of the product is the expected $[PtClPh(dpe)]$. $[PtCl_2(dpe)]$ and $[PtPh_2(dpe)]$ in equal amounts (total 60%) are present as contaminants. When this solution is treated with CO for 2 minutes at -60°C in the presence of $AgSO_3CF_3$ all $[PtClPh(dpe)]$ and $[PtCl_2(dpe)]$ disappear whilst $[PtPh_2(dpe)]$ remains intact. Only a single organoplatinum complex is noted {δ(P) +45.1 p.p.m.d J(P,Pt) 1631Hz and δ(P) +41.4 p.p.m.d 3131Hz, ^{2}J(P,P) 10.3Hz } as 40% of the product intensity. $[PtCl(CO)(dpe)]SO_3CF_3$ and $[PtPh_2(dpe)]$ are present in equal

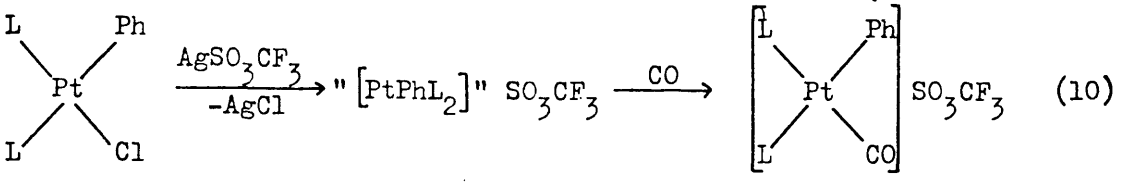
proportions totalling 60% of the total signal intensity. When the mixture was warmed to room temperature much black precipitate developed and a ^{31}Pn.m.r. spectrum of the filtered solution required overnight accumulation because it was now very dilute. This revealed a single species {δ(P) +35.9p.p.m. J(P,Pt) 3978Hz} namely $[Pt_2(\mu\text{-}Cl)_2(dpe)_2](SO_3CF_3)_2$ (which was also obtained independently from the reactions of $[PtCl_2(dpe)]$ with CO and $AgSO_3CF_3$) and no organoplatinum species.

This unknown diphos complex has n.m.r. data which suggest that the chelate phosphorus nuclei are <u>trans</u> to carbon monoxide, and an aryl or alkyl group respectively. The likely contenders for these parameters are $[PtPh(CO)(dpe)]SO_3CF_3$ and $[Pt(COPh)(CO)(dpe)]SO_3CF_3$, and although at these temperatures the phenyl complex is favoured by comparison with analogous PPh_3 and $PMePh_2$ reactions, a benzoyl complex is not entirely unlikely without more detailed proof. Whatever product either complex has given upon warming to room temperature, it has decomposed prior to spectroscopic examination of the sample, but it is formed much more rapidly at -60°C than are the monodentate phosphine derivatives.

The unknown <u>cis</u>-bis phosphine complexes formed from the reaction of <u>cis</u>-$[PtClPhL_2]$ (L = PPh_3, $PMePh_2$) or $[PtClPh(dpe)]$ with CO and $AgSO_3CF_3$ at -60°C are not observed in the absence of the silver salt. If these species are <u>cis</u>-$[Pt(Ph)(CO)(L)_2]^+(SO_3CF_3)$ or $[PtPh(CO)(dpe)]\ SO_3CF_3$ either the chloride analogues are unstable at -60°C and sufficient concentration of the cation accumulates only if the chloride is removed (equation 9), or the $AgSO_3CF_3$ reacts with the starting material to give a new reactive species which is carbonylated readily (equation 10) by the excess CO in the system.

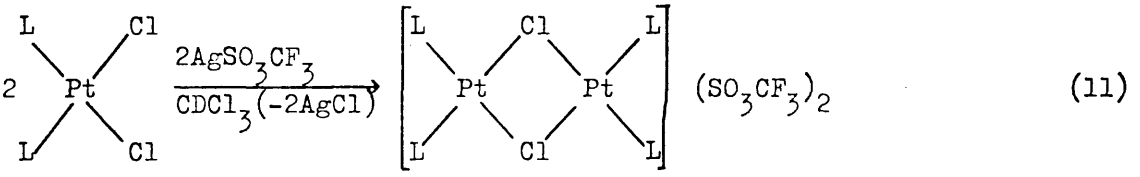


(9)



(10)

It is important to note that the reaction of cis-$[PtClPhL_2]$ and CO at $-60^{o}C$ reaches completion more quickly when $AgSO_3CF_3$ is present, and a silver ion's ability to abstract covalently bound chloride has been reported.[170] Its effect on cis-$[PtCl_2L_2]$ (L = $PMePh_2$, PMe_2Ph, PEt_3) at $+30^{o}C$ have also been observed (equation 11), Chapter 3.



(11)

^{31}P- signals for cis $[PtClPh(PMePh_2)_2]$ are broadened somewhat at $-60^{o}C$ in the presence of excess $AgSO_3CF_3$ in $CDCl_3$ ether (5:1) and two new species appear in low concentration after 20 minutes {δ(P) -4.8 p.p.m.d -11.8p.p.m.d $^{2}J(P,P)$ 14.3Hz (4%); δ(P) +11.2p.p.m.d and -5.9p.p.m. $^{2}J(P,P)$ 14.7Hz (1%), no $^{1}J(P,Pt)$ information resolved}. The precise natures of these unknowns are difficult to determine without phosphorus-platinum coupling constant information. It is not inconceivable that the signals could belong to the solvento-complex cis $[PtPh(S)(PMePh_2)_2]SO_3CF_3$ (S = $CDCl_3$), ether and the coordinatively unsaturated 'cis'-$[PtPh(PMePh_2)_2]SO_3CF_3$. Whichever route to halide abstraction is operative, $AgSO_3CF_3$ does react with cis-$[PtClPh(PMePh_2)_2]$ to a small extent and probably attacks cis-$[PtClPh(PPh_3)_2]$ and $[PtClPh(dpe)]$ in a similar fashion.

One might expect that since trans-$[PtPh(CO)L_2]^+$ ($L = PPh_3$, $PMePh_2$) as the chloride salt is stable at -60°C in the simple carbonylation reactions (with and without sulphur, but without $AgSO_3CF_3$), the corresponding cis-isomer would behave similarly. The fact that these cis species are not observed in these reactions strongly favour silver ion abstraction of covalently bound chloride from cis-$[PtClPhL_2]$ followed by rapid carbonylation to give cis-$[PtPh(CO)L_2]SO_3CF_3$. Therefore the carbonylation reactions of cis-$[PtClPhL_2]$ with and without sulphur are not of the same type as those with $AgSO_3CF_3$, although partial conversion to isomer I species and $[PtPhL_3]^+$ (or its PPh_3 alternative) is observed in both types of experiment.

If we now examine the possibility that the major cis- complexes obtained in the $AgSO_3CF_3$ treated carbonylation reactions, the benzoyl complexes cis-$[Pt(COPh)(CO)L_2]SO_3CF_3$ ($L = PPh_3$, $PMePh_2$) two factors arise which are not in their favour. Firstly, typical isomer I complexes do not react with tertiary phosphine at -60°C in the presence of $AgSO_3CF_3$ to produce cis complexes other than $[PtClRL_2]$, nor do these reactions produce any trans-$[Pt(COR)(CO)L_2]SO_3CF_3$ upon warming to room temperature. This could, of course, reflect the presence of only at most one equivalent of CO in the reactions, and not an excess, as is typical during carbonylation. Secondly, if the precursor of a complex like cis-$[Pt(COPh)(CO)\ L_2\ ]SO_3CF_3$ spontaneously inserted by a process not too dissimilar from that by which insertion at $[PtClPh(CO)L]$ ($L = PR_3$ or AsR_3 trans to Ph) operates, it might also not occur at -60°C.

Taking all of the factors discussed with respect to the carbonylation of cis$[PtClPhL_2]$ ($L = PMePh_2$, PPh_3, ½dpe) at -60°C, and the effects upon

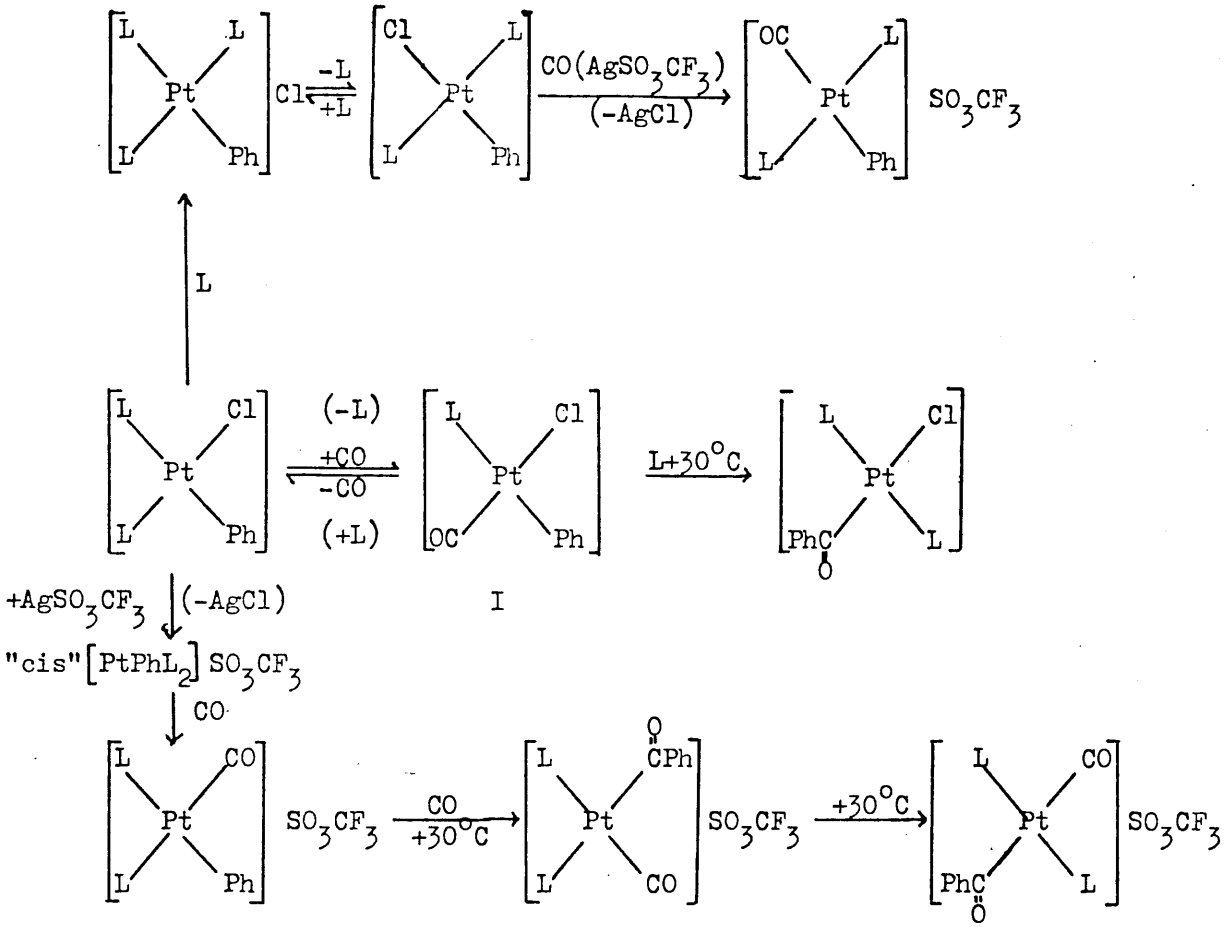
typical reaction mixtures that are apparent when they are warmed to room temperature, it is possible to construct a rudimentary reaction scheme (Scheme III). N.M.R. spectroscopic parameters for the acyl and carbonyl complexes are given in Table 17. Several aspects of the scheme which are important are:

(i) trans-$[PtPh(CO)L_2]^+X^-$ (X = Cl or SO_3CF_3) appears at -60°C from the reaction of trans-$[PtClPh(L)_2]$ with CO, and not from the isomerisation of cis $[PtPh(CO)L_2]^+X^-$. Such isomerisations would probably involve more than one nucleophilic displacement as individual steps and would therefore be slow at -60°C, although for the reaction of the PPh_3 derivatives a route involving pseudorotation of five-coordinate intermediates might be favoured.

(ii) Insertion does not occur at -60°C, but the conversion of cis-$[PtPh(CO)L_2]^+SO_3CF_3$ to trans-$[Pt(COPh)(CO)L_2]SO_3CF_3$ upon warming to +30°C is total, whilst the reaction of isomer I $[PtClPh(CO)L]$ and tertiary phosphine involves CO loss as well as insertion upon warming.

(iii) Cis-$[PtClPhL_2]$ and isomer I may readily interconvert at -60°C but the removal of the displaced phosphine as it reacts with cis-$[PtClPhL_2]$ slightly more rapidly than it does with isomer I maintains a significant concentration of the latter.

(iv) Overall rapid isomerisation of cis-$[PtClPhL_2]$ to the trans form by CO at -60°C proceeds via the formation of isomer I and $[PtPhL_3]^+Cl^-$. The latter species or its PPh_3 equivalent loses tertiary phosphine slowly at -60°C to give trans-$[PtClPhL_2]$ and further quantities of a tris-phosphine complex are generated to continue the cycle until all cis-$[PtClPhL_2]$ is exhausted.


L
L
Pt
L
Ph
Cl
-L
+L
Cl
L
Pt
L
Ph
CO(AgSO3CF3)
(-AgCl)
OC
L
Pt
L
Ph
SO3CF3
L
L
Cl
Pt
L
Ph
(-L)
+CO
-CO
(+L)
L
Cl
Pt
OC
Ph
I
L+30°C
L
Cl
Pt
PhC
O
L
+AgSO3CF3
(-AgCl)
"cis"[PtPhL2] SO3CF3
CO
L
CO
Pt
L
Ph
SO3CF3
CO
+30°C
O
CPh
L
Pt
L
CO
SO3CF3
+30°C
L
CO
Pt
PhC
O
L
SO3CF3

SCHEME III

It is proposed that the isomerisation of cis-$[PtClPhL_2]$ by CO at room temperature proceeds by this mechanism. Since no CO is incorporated to give benzoyl products the isomer I complexes must react with the phosphine released from the tris-phosphine complexes more rapidly to lose CO than they can spontaneously insert.

Finally in Scheme III it is possible that many of the nucleophilic substitutions proposed may be solvent assisted to some extent, and this aspect of the reactions has not been investigated.

The Reactions of cis-$[PtClPh(PR_3)_2]$ with Phenyl Isonitrile

The reaction at -60°C of cis-$[PtClPh(PMePh_2)_2]$ with phenyl-isonitrile in the presence of $AgSO_3CF_3$ provides interesting comparisons with the analogous room temperature reaction of trans-$[PtClPh(PMePh_2)_2]$ and intriguing contrasts with the carbonylations of the cis-complexes.

A precooled (-60°C) $CDCl_3$ solution of one equivalent of phenyl-isonitrile was added quickly by pipette to a $CDCl_3$:ether (5:1) solution of cis-$[PtClPh(PMePh_2)_2]$ which had been allowed to react with excess $AgSO_3CF_3$ (ca 3-4 equivalents) for 30 minutes at -60°C. A ^{31}Pn.m.r. spectrum recorded at this temperature soon after mixing showed there to be three major products, as well as unreacted starting material (8%). The already identified isomer I complex $[PtClPh(CNPh)(PMePh_2)]$ (P trans to Ph) (21%) and two cis bis phosphine complexes {complex A: δ(P) +0.6p.p.m.d $^1J(P,Pt)$ 3169Hz, -4.1p.p.m.d $^1J(P,Pt)$ 1660Hz, $^2J(P,P)$ 22.5Hz 25%; and complex B: δ(42%}5.9p.p.m.d $^1J(P,Pt)$ 3949Hz, +5.3p.p.m.d $^1J(P,Pt)$ 1741Hz, $^2J(P,P)$ 14.7Hz 42%} formed the bulk of the products. Two unknown resonances in equal

intensity {δ(P) -1.5p.p.m. and -4.9p.p.m. no P-Pt coupling information, total intensity 4%} were also recorded.

After warming the sample to +20°C for five minutes followed by rapid cooling to -60°C [$PtPh(PMePh_2)_3$](SO_3CF_3) appeared, and as expected it represented the same concentration as isomer I (together totalling 26%). Complexes A and B now formed 15% and 35% respectively of the total signal intensity whilst a new, but unresolved, bis phosphine species had grown {δ(P)s -0.6p.p.m.d and -14.3p.p.m.d, $^2J(P,P)$ 21.1Hz ca 14%, complex C, no $^1J(P,Pt)$s resolved} and no starting material remained. Another new product {δ(P) +7.9p.p.m. $^1J(P,Pt)$ 2937Hz} in low concentration (4%) had resulted from the brief heating. Figure 3 is the resultant ^{31}Pn.m.r. spectrum obtained at this stage.

The sample was allowed to come slowly to room temperature overnight. Complexes B and C were present as 12% and 18% respectively of the total product concentration, and the major product was [$PtPh(PMePh_2)_3$] SO_3CF_3 (31%), whilst A had disappeared and the unknown at δ(P) +7.9p.p.m. now appeared as 19% of the products at +30°C.

Isomer I [$PtClPh(CNPh)(PMePh_2)$] (P *trans* to Ph) 9% and *trans* [$PtPh(CNPh)(PMePh_2)$] SO_3CF_3 11% as well as an unknown {δ(P) -11.1p.p.m. $^1J(P,Pt)$ unresolved} were the other products in what was now a wine red coloured solution.

The rate of isomerisation of these *cis* species is indeed slow in comparison with the carbonylation reaction *cis* intermediates, but this may be a reflection on the paucity of free ligand in the isonitrile reaction in contrast to the excess of CO of the carbonylations. Carbon monoxide catalysed isomerisations are not uncommon.[144]

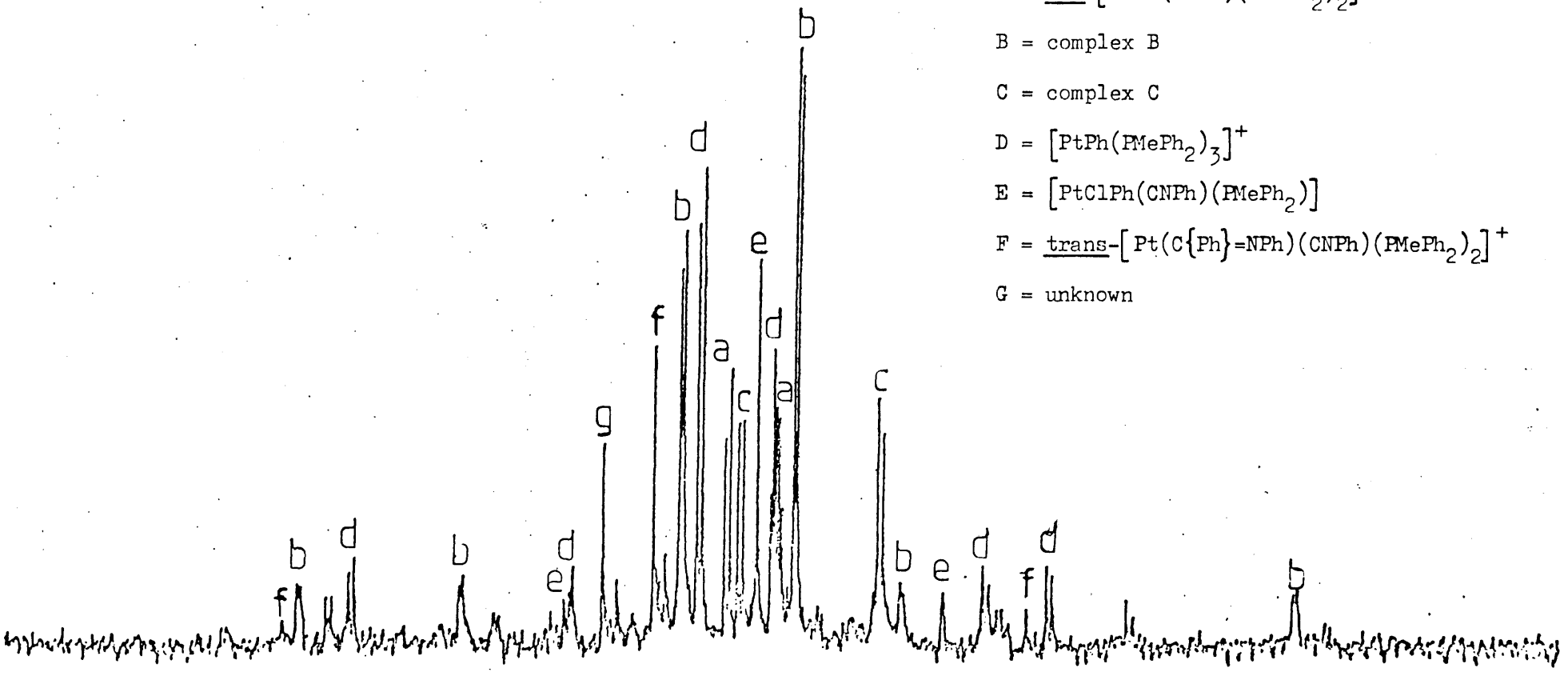
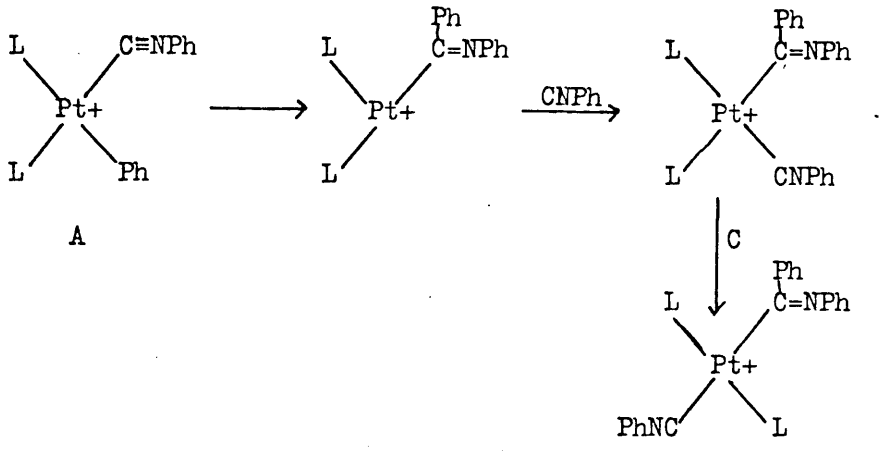

A = cis-[PtPh(CNPh)(PMePh2)2]+
B = complex B
C = complex C
D = [PtPh(PMePh2)3]+
E = [PtClPh(CNPh)(PMePh2)]
F = trans-[Pt(C{Ph}=NPh)(CNPh)(PMePh2)2]+
G = unknown

FIG 3

Complex A has spectroscopic parameters similar to the unknown cis complexes, tentatively assigned as cis $[PtPhCOL_2]SO_3CF_3$, apparent from the $AgSO_3CF_3$ treated carbonylation of cis$[PtClPhL_2]$ (L = $PMePh_2$, PPh_3). Very little information is available about the $^1J(P,Pt)$ of Ph_2MeP trans to CNPh in complexes such as this but $[PtClPh(CNPh)(PMePh_2)]$ (P trans to CNPh) has a $^1J(P,Pt)$ of 3368Hz and if we assign A as cis-$[PtPh(CNPh)(PMePh_2)_2]SO_3CF_3$ it is possible that the cis influence of the other phosphine (trans to Ph) could lower the coupling to the value we observe for A (3169Hz). A, like its CO analogue, does not survive at room temperature, whilst the latter complex converts to trans-$[Pt(COPh)(CO)(PMePh_2)_2]SO_3CF_3$. A appears to be replaced by a signal at $\delta(P)$ +7.9p.p.m. $^1J(P,Pt)$ 2937Hz and it too is only produced upon warming. Although the coupling constant of this species is ca 150Hz bigger than it is for the benzoyl complex, it is assigned as trans-$[Pt\{C(Ph)=NPh\}(CNPh)(PMePh_2)_2]SO_3CF_3$.

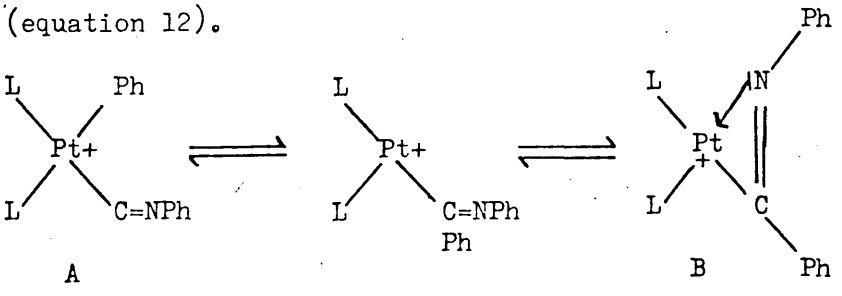
Complex C cannot reliably be assigned without more detailed coupling constant information. However, the $^2J(P,P)$ value of 21.1Hz that it has is in the same range of values as those of complex A and cis-$[Pt(COPh)(CO)(L_2)]SO_3CF_3$. Therefore although $^2J(P,P)$-cis are less sensitive to changes in the ligand environment it is proposed that the phosphines is C are trans to an aryl group and an isonitrile respectively. Finally, because C appears only after heating to room temperature the organic group is presumed to be an iminoacyl fragment and C is therefore tentatively assigned as cis-$[Pt\{C(Ph)=NPh\}(CNPh)(PMePh_2)_2]SO_3CF_3$. Complex C and trans-$[Pt\{C(Ph)=NPh\}(CNPh)(PMePh_2)_2]SO_3CF_3$ together represent 28% of the total product containing as proposed two isonitriles per metal, therefore it is reassuring that an almost equal proportion (31%) of the products

do not contain isonitrile, as $PtPh(PMePh_2)_2\ SO_3CF_3$. A, C and the trans-complex (D) are related according to Scheme IV.



SCHEME IV

The $^1J(P,Pt)$ values of the phosphines in complex B are suggestive of one phosphine being trans to an organic moeity ($^1J(P,PT)$ 1741Hz) whilst the other is trans to a ligand of low trans influence, but not chloride. (cis-$[PtClPh(PMePh_2)_2]$ is already identified and cis $[PtCl(C\{Ph\}=NPh)(PMePh_2)_2]$ appears in the reaction of trans-$[PtClPh(PMePh_2)_2]$ and CNPh.) Mass balance considerations of the remainder of the products suggest that B has one isonitrile ligand per metal. Accordingly this remaining ligand site could be occupied by the nitrogen lone pair of an iminoacyl fragment given that insertion had occurred at -60°C. B and the three-coordinate iminoacyl species of Scheme IV could possibly be related as shown (equation 12).

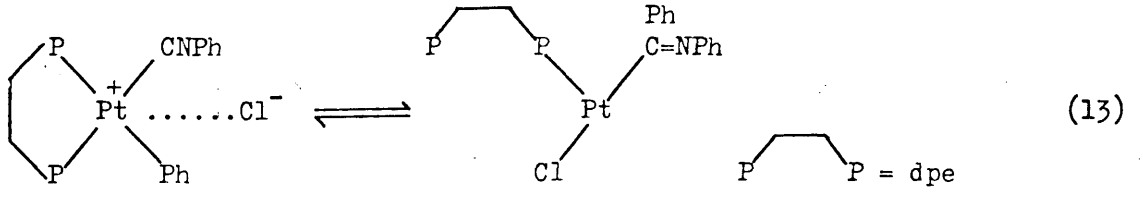


(12)

Iminoacyl chelates such as this are known,[171] but they are more commonly formed from multiple inserted insonitriles[118] at NiII and PdII.

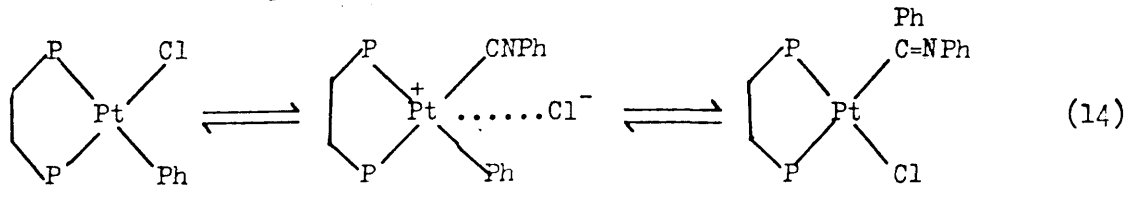
A slight deficiency of CNPh (neat) reacts at room temperature with a $CDCl_3$ solution of [PtClPh(dpe)] (dpe = 1.2 bisdiphenylphosphinoethane) (prepared from [PtClPh(cod)] and dpe) to produce a single species {δ(P)s +33.7p.p.m.d and +34.6p.p.m.d, $^1J(P,Pt)$'s 4180 and 1685Hz respectively, $^2J(P,P)$ 5.8Hz}. One end of the chelate ligand is trans to a σ-bonded organic group whilst the other is trans to Cl^-. A solution infrared spectrum $2400cm^{-1}$-$1300cm^{-1}$ of this same mixture a short while later in $CHCl_3$ exhibits no terminal isonitrile stretching bands. This is suggestive of complete insertion, although no strong iminoacyl-bands could be identified in the region $1500-1650cm^{-1}$. A ^{31}Pn.m.r. spectrum recorded upon reapplication of $CDCl_3$ is unchanged. Both the infrared data of this sample and the close similarity of the unknown's n.m.r parameters with [PtClPh(dpe)] itself, strongly favour the assignment of this product as [PtCl{C(Ph)=NPh}(dpe)]

In this reaction it is obvious that the expected intermediate $[PtPh(CNPh)(dpe)]^+Cl^-$ can neither isomerise (chelate diphos ligands that can span trans- positions have longer chain lengths) nor can it easily dissociate a phosphine link to give an isomer I. The same geometry difficulties would be encountered in the second case. If insertion proceeded by the expected route a site would become vacant trans to the coordinated end of the dpe after insertion (equation 13). Realistically only two courses of action



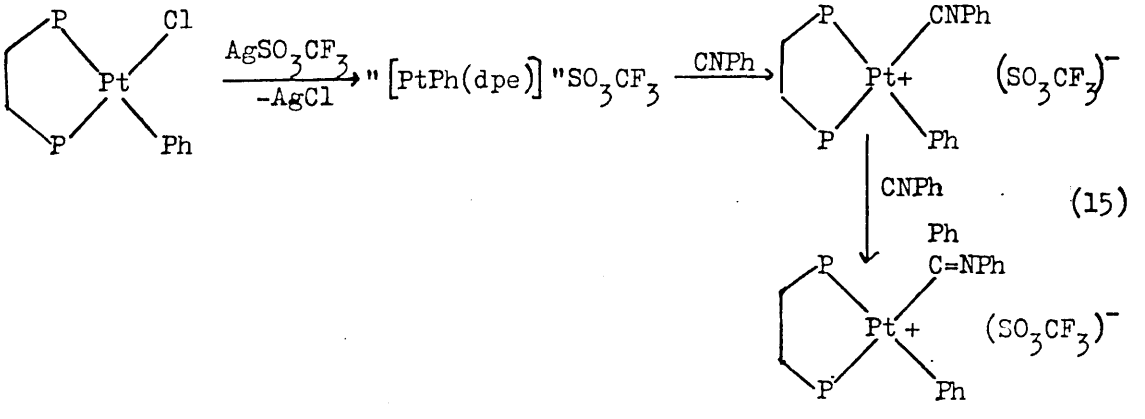
(13)

are open to this intermediate: (i) it can insert to give [PtCl(C{Ph}=NPh)dpe] or (ii) it can lose CNPh to return to starting material. It is the former pathway that operates (equation 14).



(14)

If $AgSO_3CF_3$ is present during the reaction of [PtClPh(dpe)] and CNPh in $CDCl_3$ at +20°C a new species appears immediately {δ(P) +46.5p.p.m.d and +41.8p.p.m.d, ^1J(P,Pt)s 1560 and 3140Hz respectively, ^2J(P,P) 6.6Hz} and starting material is the only other component of the resultant mixture, ca 50%. Whilst the ^{31}P-^{195}Pt coupling parameters of this complex are very similar to those assigned to cis-$[PtPh(CNPh)(PMePh_2)_2]$ SO_3CF_3 and its carbonyl analogues; however, one full equivalent of the isonitrile has been added and yet half of the spectrum is starting material. This would suggest that this complex contains two isonitrile ligands per metal. If the new signal does correspond to $[Pt\{C(Ph)=NPh\}(CNPh)(dpe)]SO_3CF_3$ then it would be purely coincidental that its ^1J(P,Pt) values are close to those of the analogous $PMePh_2$ complex. However, no decomposition of the reaction mixture was visible as might be expected were this complex $[PtPh(CNPh)(dpe)]SO_3CF_3$, therefore it must be the iminoacyl complex $[Pt(C\{Ph\}=NPh)(CNPh)(dpe)]SO_3CF_3$. This assignment would fit with rapid insertion at room temperature from $[PtPh(CNPh)(dpe)]SO_3CF_3$, which was faster than the reaction of [PtClPh(dpe)] with CNPh. $AgSO_3CF_3$ probably initiates the reaction by abstracting a halide from the [PtClPh(dpe)] (equation 15) although this has not been investigated.



(15)

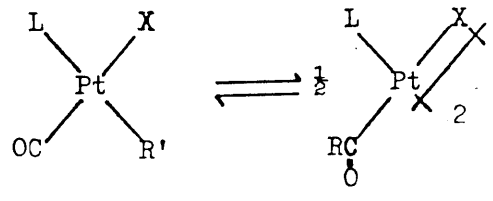
Conclusion

From the reactions performed thus far, phenyl isonitrile can be said to

react with cis-$[PtClPhL_2]$, ($L = PMePh_2$, PPh_3 or L_2 = dpe) by a mechanism similar to Scheme III at low temperatures. One very important difference however for the $PMePh_2$ complexes at least, is the far slower rate of isomerisation of the cis-bis phosphine isonitrile and iminoacyl intermediates, than their carbonyl analogues. This is an important difference and it has bearing on a possible extra pathway in the overall carbonylation mechanism of trans-$[PtXR'L_2]$ ($L = PR_3$, R' = organic group). Heck and co workers have reported[168] the operation of both a dissociative and an associative route to the acyl-complexes whilst Cross and Anderson have elucidated[51] the mechanism of the dissociative route, which Heck had established as the major route. Neither group of workers have suggested the intermediacy of cis bisphoshine carbonyl or acyl species.

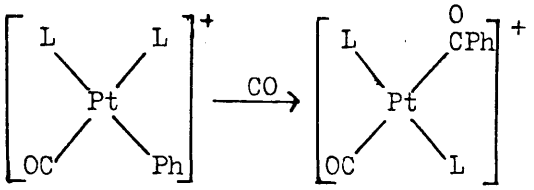
If the mechanisms for the reaction of trans-$[PtClPhL_2]$ with CNR and CO are essentially the same, as they appear to be for the cis complexes, it is possible that the cis intermediates of the isonitrile reaction (which are seen to isomerise very slowly) have carbonyl and benzoyl analogues. These analogues, because they isomerise very rapidly at room temperature during carbonylation, have not yet been detected. Perhaps by examining the reaction of trans-$[PtXR'L_2]$ with CO at a lower temperature (to inhibit isomerisation of the intermediates) it will be possible to investigate this possibility.

The conditions which govern spontaneous insertion at PtII in the complexes $[PtXR'(CO)L]$ (R' trans to L, X = halide, R' = organic group, $L = PR_3$, AsR_3) (equation 16) are now more generally applicable to salts of the cation



(16)

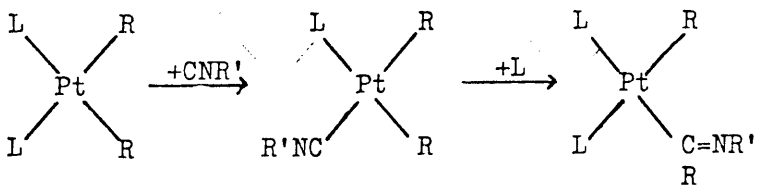
cis-$[PtPh(CO)L_2]^+$. The triflate salt of this cation, although not having a bridging halide, inserts cleanly and isomerises upon warming to room temperature (equation 17). The possible bond weakening cis



(17)

influence of the tertiary phosphine L on the metal-phenyl δ-bond might make insertion in complexes such as these more facile than it is in an isomer I situation. It is probably for this reason that insertion of CO into the complex $[PtClPh(dpe)]$ is rapid at room temperature.

Clark and coworkers[172] observed an enhancement of insertion reactions in cationic platinum complexes relative to analogous uncharged species, and such a phenomenon could be operating in this particular carbonyl system. It is certainly interesting to speculate upon the range of ligands instead of X = halide, such as phosphine, arsine, CO, amine or organic group, which might expand the number of insertion situations at platinum. Related to this are the insertion reactions reported by Treichel and Wagner[148] when cis-$[PtR_2L_2]$ (R = Me,Ph, L = tertiary phosphine) are treated with CNR' (R' = Me, $pClC_6H_4$) to give cis-$[PtR(C\{R\}=NR')L_2]$. The complexes cis-$[PtR_2(CNR')L]$, which are related to an isonitrile isomer I situation where X = R, occur as intermediates (equation 18).



(18)

From the reactions of trans-$[PtClPh(PMePh_2)_2]$ with CNR (R = Me,Ph) it was observed that whilst both methyl- and phenyl-isonitriles could form

TABLE 15

^{31}Pn.m.r. Parameters of Organoplatinum Complexes

	$\delta(P)$[a]/p.p.m.	$^{1}J(P,Pt)$/Hz	$^{2}J(P,P)$/Hz
cis-$[PtClPh(PMePh_2)_2]$	+4.3(d)[b]	1631	15.2
	+0.2(d)	4369	
cis-$[PtCl(oMeO\text{-}C_6C_4)(PMePh_2)_2]$	+5.4(d)	1735	16.3
	-1.1(d)	4336	
cis-$[PtClPh(PPh_3)_2]$	+20.4(d)	1559	14.5
	+18.0(d)	4528	
cis-$[PtCl(pNC\text{-}C_6H_4)(PPh_3)_2]$	+19.4(d)	1658	15.3
	+17.3(d)	4371	
trans-$[PtCl(oMeO\text{-}C_6H_4)(PMePh_2)_2]$	+8.3	2988	
trans-$[PtClPh(PPh_3)_2]$	+24.9	3133	
trans-$[PtCl(pNC\text{-}C_6H_4)(PPh_3)_2]$	+24.4	3024	
cis-$[PtPh_2(PMePh_2)_2]$	+1.2	1763	
cis-$[PtPh_2(PPh_3)_2]$	+19.1	1750	
$[PtPh(PMePh_2)_3]SO_3CF_3$(or Cl)	-3.7(t)	1796	21.1
	+3.1(d)	2800	
$[Pt(oMeO\text{-}C_6H_4)(PMePh_2)_3]SO_3CF_3$	-4.6(t)	1744	22.1
(or Cl)	+2.7(d)	2757	

(a) Relative to 85% H_3PO_3 at +30°C: positive shifts are downfield.

(b) d = doublet; t = triplet

TABLE 16

^{31}Pn.m.r. Parameters of Organoplatinum Carbonyl Complexes

	$\delta(P)^{(a)}$/p.p.m.	$^1J(P,Pt)$/Hz	$^2J(P,P)$/Hz
trans-$[PtPh(CO)(PMePh_2)_2]SO_3CF_3$	+3.8	2549	
trans-$[Pt(p\text{-}MeO\text{-}C_6H_4)(CO)(PMePh_2)_2]SO_3CF_3$	+3.8	2462	
cis-$[PtPh(CO)(PMePh_2)_2]SO_3CF_3$ (b)	-4.0(d)	1787	24.3
	-0.3(d)	3296	
trans-$[PtPh(CO)(PPh_3)_2](SO_3CF_3)$	-16.0	2627	
trans-$[Pt(pNC\text{-}C_6H_4)(CO)(PPh_3)_2]SO_3CF_3$	-15.9	2643	
cis-$[PtPh(CO)(PPh_3)_2]SO_3CF_3$ (b)	+11.5(d)	1667	23.0
	+19.5(d)	3470	
$[PtPh(CO)(dpe)]SO_3CF_3$	+45.1(d)	1631	10.3
	+41.4(d)	3131	
trans-$[Pt(COPh)(CO)(PMePh_2)_2]SO_3CF_3$	-1.0	2782	
trans-$[Pt(COPh)(CO)(PPh_3)_2]SO_3CF_3$	+13.5	2954	
trans-$[PtCl(COPh)(PMePh_2)_2]$	+5.2	3211	
trans-$[PtCl(o\text{-}MeO\text{-}C_6H_4\text{-}CO)(PMePh_2)_2]$	+5.8	3276	
trans-$[PtCl(COPh)(PPh_3)_2]$	+20.3	3335	

(a) In $CDCl_3$:ether (5:1) at +30°C relative to 85% H_3PO_4: positive shifts are downfield. (d) = doublet.

(b) Recorded at -60°C.

TABLE 17

Spectroscopic Data for cis-$[PtCl_2(CO\text{-}C_6H_4\text{-}Y)(PMePh_2)]^-$ (a)

Y	δP (b) /p.p.m.	$^1J(P,Pt)$	$\nu(CO)$ (c) /cm^{-1}
o-Me	-6.0	5106	1615
p-H	-5.3	4946	1612
p-CO_2Me	-5.3	4898	1611
p-CN	-6.0	4884	1614

(a) Salts of Et_4N^+

(b) In $CDCl_3$ relative to 85% H_3PO_4 at +30°C.

(c) Recorded as 0.02 molar $CHCl_3$ solutions in 0.5mm spacing NaCl solution cells.

ionic complexes by substitution of the halide, only the phenyl-isonitrile complex gave insertion products after a long period of time. This tendency may reflect the relative stabilities of the products of methyl- or phenyl-isonitrile insertion respectively. Certainly one would expect greater resonance stabilisation for a phenyl-iminoacyl ligand than for the methyl derivative, and this may be an important factor.

Experimental

Phosphorus-31 N.M.R. specra were recorded using a Varian XL100 spectrometer (100MHz) operating in the Fourier Transform mode. The temperatures of the recordings are accurate to $\pm$ 5°C at -60°C. Solution infrared spectra were recorded using a P.E. 557 spectrometer as 0.02 molar chloroform solutions in 0.5mm spacing NaCl cells. The complexes $[PtClPhL_2]$ ($L = PMePh_2$, PPh_3 and $L_2 = Ph_2PCH_2CH_2PPh_2$) were prepared in situ by adding the appropriate quanitity of 0.54N ethereal HCl to $CDCl_3$ solutions of $[PtPh_2L_2]$ at -60°C. Typically the solutions were 90-95% cis product with small quantities of cis$[PtCl_2L_2]$, $[PtPh_2L_2]$ and trans-$[PtClPhL_2]$ as contaminants. Attempted recrystallisation of cis-$[PtClPhL_2]$ gave the microanalytically pure trans isomers (identified by infrared analysis). KBr infrared spectra 4000-200cm^{-1} of the crude solids were similar to trans $[PtClPhL_2]$ except for a general broadening of the peaks associated with L and a shift in ν(Pt-Cl): $L = PMePh_2$ trans 287cm^{-1}, cis 301cm^{-1}: $L = PPh_3$ trans 286cm^{-1}, cis 304cm^{-1}. L_2 = dpe 303cm^{-1}.

Isomerisation of cis-$[PtClPh(PPh_3)_2]$ in $CDCl_3$/ether solution:

A $CDCl_3$/ether (5:1) solution of cis-$[PtClPh(Ph_3P)_2]$ (92%) containing the

trans isomer (4%), cis-$[PtPh_2(PPh_3)_2]$ (3%) and cis-$[PtCl_2PPh_3)_2]$ (1%) was left for 24 hours at room temperature. After this time a ^{31}Pn.m.r. spectrum revealed the following composition: cis-$[PtClPh(PPh_3)_2]$ 88%, trans isomer 7%, cis-$[PtPh_2(PPh_3)_2]$ 3% and cis-$[PtCl_2(PPh_3)_2]$ 2%.

Preparation of Chloro(orthomethoxyphenyl)carbonyl(diphenylmethylphosphine)-platinum isomer I:

Bis (o-methoxyphenyl) mercury (111mg. 0.26m mols) was dissolved in a $CDCl_3$ solution (13.5mls) of cis-$[PtCl_2(CO)(PMePh_2)]$ (123mgs 0.25m mols) and left stirring for four days. Solution infrared spectra of the mixture during this period recorded the gradual appearance of a ν(CO) of 2195 cm^{-1} for the product as that for the starting material (2115cm^{-1}) decreased in intensity. A ^{31}Pn.m.r. spectrum recorded after four days showed that this reaction had gone to completion to give a single product, namely $[PtCl(oMeO\text{-}C_6H_4)(CO)(PMePh_2)]$ isomer I (R trans to phosphine) {δ(P) +7.1p.p.m., J(P,Pt) 1534Hz}. A quantity of o-methoxyphenyl mercuric chloride (80 mg. ca 95%) was removed upon filtration and the remainder upon reducing the volume of the liquors. Aliquots of the solution after dilution (0.02 molar in $CHCl_3$) were used in ^{31}Pn.m.r. experiments after replacing the solvent with $CDCl_3$ or CH_2Cl_2:$CDCl_3$ (1:1).

Preparation of Chloro(para-cyanophenyl)carbonyl(triphenylphosphine)platinum:

Prepared similarly to above from cis $[PtCl_2(CO)(PPh_3)]$ and bis(paracyanophenyl) mercury in $CHCl_3$ in 30 minutes. All the paracyanophenyl-mercuric chloride is removed by filtration. The solution was used without further purification (for ^{31}Pn.m.r. experiments the $CHCl_3$ was removed by rotary evaporation and replaced by $CDCl_3$).

The Reactions of $[PtCl(Y\text{-}C_6H_4)(CO)(PMePh_2)]$ isomer I (various Y) with $Et_4N^+Cl^-$

cis-$[PtCl_2(CO)(PMePh_2)]$ (typically 20mg) was treated with one equivalent of $(Y\text{-}C_6H_4)_2Hg$ (Y = p-H, pCO_2Me, oMeO, o-methyl) and after leaving to react (30 minutes for para Y, 3-4 days for oortho Y) one equivalent of $Et_4N^+Cl^-$ was added to the reaction mixture at room temperature. ^{31}Pn.m.r. spectroscopic examination confirmed that the reaction had given single products δ(P) -5.3 — -6.0p.p.m., ^1J(P,Pt)s 4884-5l)6Hz which solution infrared analysis confirmed as having an acyl-ligand ν(CO) 1161-1615cm^{-1}. Spectroscopic data for the complexes cis Et_4N^+ $PtCl_2(COC_6H_4\text{-}Y)(PMePh_2)$ are given in Table 17.

APPENDIX

PHOSPHORUS-31 N.M.R. SPECTRA OF

PLATINUM II COMPLEXES

Introduction

Assignments made using the ^{31}Pn.m.r. parameters of shift $\{\delta(P)\}$, one bond phosphorus-platinum 195 coupling constant $\{^{1}J(P,Pt)$, ^{195}Pt 33% I $=\frac{1}{2}\}$ and where appropriate the two bond phosphorus-phosphorus coupling $\{^{2}J(P,P)\}$ for tertiary phosphine platinum II complexes, are in some instances unambiguous.[174] The relationship between $^{1}J(P,Pt)$ and geometry for the cis and trans isomers of $[PtX_2L_2]$(X = halide, L = tertiary phosphine) has been reported.[175] Generally the ratio of Jcis (typically 3300-3600Hz) to Jtrans (usually between 2200 to 2500Hz) is ca 1.4-1.6 for a wide range of phosphines and halides.[176]

Using the phosphorus shifts of some thirty cis and trans bis-phosphine dichloride platinum complexes, and the shifts of the uncoordinated phosphines, a direct relationship has been determined,[177] (equation 1).

$$\Delta = A + B \qquad (1)$$

The change in shift upon coordination of the phosphine (Δ) is linearly related to the shift of the free phosphine (δ) by parameters A and B which are specific for each isomer. This empirical relationship is useful for providing crude estimates of the shift of new complexes. Generally the shift $\delta(P)$ of the trans isomers of $[PtX_2L_2]$ are downfield of the cis isomers (Figure 4).[176]

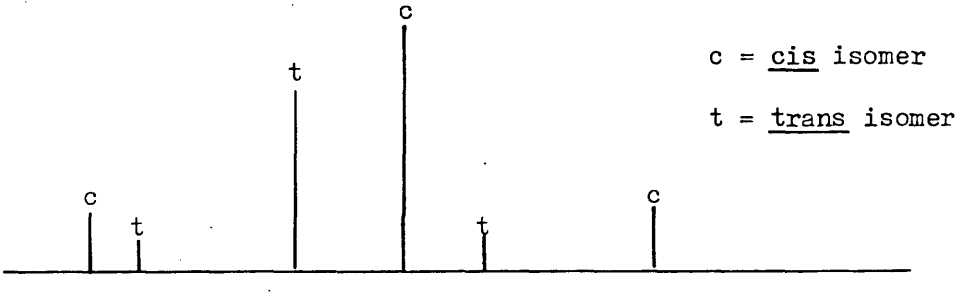


Figure 4

In general $^{1}J(P,Pt)$ values are small when phosphorus is trans to a ligand of high trans influence and large when trans to a ligand of low trans influence. N.M.R. studies[76] of a series of $[PtCl_2(L)(PBu_3)]$ and trans-$[PtCl(L)(PBu_3)_2]Cl$ have been claimed to provide data on the cis influence of tertiary phosphines. $^{2}J(P,P)$ values are approximately 20Hz between non-equivalent phosphorus nuclei that are cis in a platinum II complex.[76] The $^{2}J(P,P)$ between different tertiary phosphine-phosphorus nuclei, mutually trans, are an order magnitude larger (200-600Hz) than the cis couplings.[76]

The cis-influence of the ligands L cis to PEt_3 in $[PtCl_2(L)(PEt_3)]$ $\{L = Cl^-$ $C(NPhCH_2)_2$, CNPh, C(PEt)Nph, PEt_3, CO, $P(OPh)_3$, $PF_3\}$ has only a poor correlation with $^{1}J(P,Pt)$[75] (Table 19). A derivative of the series with L = Ph cis $Et_4N^+[PtCl_2(Ph)(PEt_3)_2]$ is prepared by adding two equivalents of $Et_4N^+Cl^-$ to $[Pt_2Cl_2Ph_2(PEt_3)_2]$ in $CDCl_3$ at room temperature, (equation 1).

$$[Pt_2Cl_2Ph_2(PEt_3)_2] + 2Cl^- \longrightarrow 2 \begin{matrix} Et_3P' & & Cl \\ & Pt- & \\ Ph & & Cl \end{matrix} \qquad (1)$$

This complex has a $^{1}J(P,Pt)$ value approximately 800Hz bigger than that of the ligand of lowest cis influence $\{\delta(P)$ +5.7p.p.m. $^{1}J(P.Pt)$ 4529Hz$\}$. Despite the poor correlation the magnitude of difference between the coupling constants of the Cl andPh derivatives would suggest that the bond cis to phenyl is shorter. However, a large $^{1}J(P,Pt)$ value in a similar situation[131] was found not to correspond to an exceptionally short Pt-P bond. Until the phenyl complex is structurally characterised, any suggestion as to the bond length must remain somewhat speculative.

From a variety of aryl and benzoyl platinum complexes in which a σ-bonding organic group is cis to one or two tertiary phosphine ligands, trends in

TABLE 19

Ligand *cis* influence and J(P,Pt) (in order of decreasing Pt-P bond length in *cis* $[PtCl_2L(PEt_3)]$)

L	$^1J(P,Pt)/Hz$
PF_3	2760
$P(OPh)_3$	3210
CO	2754
PEt_3	3515
C(OEt)NPhH	——
CNPh	3049
$C(NPhCH_2)_2$	3720
Cl	3764

$\delta(P)$ and $^{1}J(P,Pt)$ are noted with respect to substitution of benzoyl for aryl. The n.m.r. data and the parameters 'Δp' and 'r_J' are given in Tables 20, 21 and 22. Δp is the change in shift of the phosphorus nuclei (usually positive) and r_J is the ratio of $^{1}J(P,Pt)$ in the benzoyl complex to that in the aryl complex.

Δp is positive in 14 out of 15 examples and these shifts in $\delta(P)$ range from 1.6 to 7.4p.p.m. There seems to be no distinctive pattern in these values, but the changes are smaller for the dimeric platinum complexes. More significantly, the range of values for parameter r_J is narrower. For all of the examples the mean is 1.07 ± 0.02, i.e. there is on average a 7% increase in $^{1}J(P,Pt)$ for a change in substituent from phenyl to benzoyl in *trans*-$[PtXR'L_2]$ *trans*-$[PtCO(R')L_2]$ $[Pt_2X_2(R')_2L_2]$ and other complexes. Systematic parameter changes such as this can be extremely useful tools in structure determinations.

The two $^{1}J(P,Pt)$ values for the complexes *cis*-$[PtCl(R)L_2]$ (R = alkyl or aryl, L = tertiary phosphine) are reasonably uniform in magnitude for a range of R and L (Table 23). The range of values for monodentate L are 4345-4528Hz for P *trans* to Cl and 1731-1559Hz for P *trans* to Ph. For the dpe complexes the range of $^{1}J(P,Pt)$ values for P *trans* to R is included in those of the monodentate L whilst a lower range 4192-4211Hz is noted for the other phosphorus nuclei. The values of $^{2}J(P,P)$ are comparable to the signal linewidths for the dpe complexes but are much higher (14-19Hz) for the monodentate phosphine complexes. Finally the shifts $\delta(P)$ of those phosphines *trans* to R (for the ten examples quoted) are always downfield to those of phosphines *trans* to Cl, but the differences of these shifts, within each molecule, are not uniform.

TABLE 21

Comparison of $\delta(P)$ and $^1J(P,Pt)$ for $[Pt_2(\mu\text{-}X)_2Ph_2L_2]$ and $[Pt_2(\mu\text{-}X)_2(COPh)_2L_2]$ (a)(b)

		$[Pt_2(\mu\text{-}X)_2R_2L_2]$		$Pt_2(\mu\text{-}X)_2(COR)_2L_2$			
X	L	$\delta(P)$p.p.m.	$^1J(P,Pt)$/Hz	$\delta(P)$/p.p.m.	$J(P,Pt)$/Hz	Δp	r_J
Cl	PEt_3	+9.0	4757	+10.7	5041	-1.7	1.055
		+8.5	4775			-2.2	1.059
Cl	PMe_2Ph	-13.2	4817	-15.0	5180	1.8	1.070
		-13.4	4835			1.6	1.075
Cl	$PMePh_2$	-1.1	5010	-3.3	5321	2.2	1.054
		-0.9	5050			2.4	1.062
I	$PMePh_2$	-0.7	4581	-4.4	5016	3.7	1.100
		-0.9	4600	-5.1	5100	4.2	1.109
Cl	PPh_3	+13.1	5165	+11.0	5495	2.1	1.064
		+13.6	-			2.6	-

(a) See reference 178.

(b) Cis and trans isomers were observable.

TABLE 22

Miscellaneous Comparisons of $\delta(P)$ and $^1J(P,Pt)$ for Benzoyl- and Aryl- Complexes of Platinum

Complex	R	L	Aryl $\delta(P)$/p.p.m.	Aryl $^1J(P,Pt)$/Hz	Benzoyl $\delta(P)$/p.p.m.	Benzoyl $^1J(P,Pt)$/Hz	Δp	r_J
$Et_4N^+ [PtCl_2R'L_2]^-$	Ph	$PMePh_2$	-1.4	4757	-5.3	4946	3.9	1.040
	p-MeO_2C-C_6H_4	$PMePh_2$	-1.4	4665	-5.3	4898	3.9	1.052
trans-$[PtR(CO)L_2]^+$	Ph	$PMePh_2$	+3.9	2560	-1.0	2782	4.9	1.086
	Ph	PPh_3	+15.6	2656	+13.5	2954	2.1	1.113
$[PtRL_3]^+$ (a)	Ph	$PMePh_2$	+3.1	2800	-4.3	3015	7.4	1.076

(a) See reference 179.

TABLE 20

A comparison of $\delta(P)$ and $^1J(P,Pt)$ for *trans*-$[PtX(R)L_2]$ and *trans*-$[PtX(COR)L_2]$

			Aryl		Benzoyl			
X	R	L	$\delta(P)$p.p.m.	$^1J(P,Pt)$/Hz	$\delta(P)$p.p.m.	$^1J(P,Pt)$/Hz	Δp/p.p.m.	r_J
Cl	Ph	$PMePh_2$	+8.7	3010	+5.1	3215	3.6	1.068
Cl	o-$MeOC_6H_4$	$PMePh_2$	+9.2	2696	+5.8	3276	3.4	1.104
Cl	Ph	PPh_3	+24.5	3152	+19.9	3381	4.6	1.070
I	Ph	P(*p*-tolyl)$_3$ (a)	+19.9	3064	+14.9	3290	5.0	1.074
I	Ph	P(*p*-anisyl)$_3$ (a)	+18.3	3044	+13.2	3262	5.1	1.072

(a) See references 51 and 178.

TABLE 23

^{31}Pn.m.r. Parameters of cis-$[PtCl(R)L_2]$

R	L	δ(P)/p.p.m.	^1J(P,Pt)/Hz	^2J(P,P)/Hz	Ref
Ph	$PMePh_2$	+4.3	1621	15.2	this work
		+0.2	4369		
o-MeO-C_6H_4	$PMePh_2$ (a)	+6.0	1731	15.5	this work
		-0.9	4345		
Cl_2C=CCl	$PMePh_2$ (b)	-0.3	2043	18.6	this work
		-4.6	3992		
Ph	PPh_3	+20.4	1559	14.5	this work
		+18.0	4228		
p-NC-C_6H_4	PPh_3	+19.4	1651	15.5	this work
		+17.3	4371		
-C(=NC_6H_4pOMe)COMe	PPh_3	+37.6 (c)	1729	17.1	180
		+32.1	4504		
CH_2Cl	PPh_3	+20.6	1696	15.3	181
		+19.2	4463		
Ph	dpe	+38.9	1640	2.2	this work
		+37.2	4192		
p-MeO-C_6H_4	dpe	+41.1	1672	0	182
		+37.9	4166		
Me	dpe	+44.6	1738	0	182
		+43.2	4211		

(a) Recorded at -60°C.

(b) Obtained as 80% of the product in the reaction $[PtCl(Cl_2C{=}CCl)(CO)L]$ (L trans to Cl_2C=CCl) +L

(c) Measured relative to external PEt_3 standard.

Experimental

The spectral data in Tables 20, 21, 22 and 23 were recorded for $CDCl_3$ (or $CDCl_3/CH_2Cl_2$ (1:1)) solutions at +30°C (unless otherwise stated) using a Varian XL100 spectrometer operating in the Fourier Transform mode. Shifts $\delta(P)$ are relative to external 85% H_3PO_4 and positive shifts are downfield of the standard.

REFERENCES

1 W.C. Zeise, Pogg. Ann., 9 632, (1827): idem ibid 21 497, (1831)

2 E. Frankland, Annalen, 13, 71 (1849): idem J. Chem. Soc. 2, 263 (1850)

3 G.B. Buckton, Proc. Roy. Soc. 9, 309, (1859)

4 V. Grignard, Compt. Rend. 130, (1322), (1900)

5 W.J. Pope and S.J. Peachey, Proc. Chem. Soc. 23, 86 (1907): idem J. Chem. Soc. 571 (1909)

6 W.S. Schlenk, J. Appenrodt, A. Michael and A. Thal, Ber. Chem Ges. 47, 473 (1914)

7 K. Ziegler and H. Colonius, Annalen 479, 135 (1930)

8 J. Chatt and B.L. Shaw, J. Chem. Soc. 705, (1959): idem ibid 4020 (1959)

9 J. Chatt and B.L. Shaw, J. Chem. Soc. 5075, (1962)

10 B.N. Figgis, J. Lewis, R.F. Long, R. Mason, R.S. Nyholm, P.J. Pauling and G.B. Robertson, Nature 195, 1278 (1962)

11 C.R. Kistner, J.H. Hutchinson, J.R. Doyle and J.C. Storlie, Inorg. Chem. 2, 1255 (1963)

12 A.D. Westland and M. Northcott, Can. J. Chem. 48, 2907 (1970): C.R. Kistner, J.D. Blackman and W.C. Harris, Inorg. Chem. 8, 2165, (1969)

13 J.A. Osborne, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, 1711 (1966)

14 For examples see J. Halpern, Pure Applied Chem. 51, 2171 (1979) and references therein, J. Chatt et al, Catalysis, Progress in Research, eds. F. Basalo and R. Burwell, Plenum Press, New York, pp 107-129 (1973)

15 N.V. Sidgewick, The Electronic Theory of Valence, Oxford University Press, London, 1929, p 163

16 P.S. Bratermann and R.J. Cross, Chem. Soc. Rev., 2, 271 (1973)

17 E. Singleton, J. Organometallic Chem., 158, 413 (1978)

18 C. Tolman, W.C. Seidel and D.H. Gerlach, J. Amer. Chem. Soc., 94 2669 (1972)

19 E.H. Brooks and R.J. Cross, Organometallic Chem. Revs., A, 6, 227 (1970)

20 D.P. Rice and J.A. Osborn, J. Organometallic Chem., 30, C84 (1974)

21 M.L.H. Green and R. Mahtab, J.C.S. Dalton, 262 (1979): J.X. McDermott, M.E. Wilson and G.M. Whitesides, J. Amer. Chem. Soc., 98, 6529 (1976): F.G.N. Cloke and M.L.H. Green, J.C.S. Chem. Comm., 127 (1979)

22 C.A. Tolman, Chem. Soc. Rev., 1, 337 (1972) and references therein

23 R.J. Mawby, F. Basolo and R.G. Pearson, J. Amer. Chem. Soc., 86, 3994 (1964)

24 F.R. Hartley, The Chemistry of Platinum and Palladium, Applied Science Publishers, London, (1973)

25 R. Ugo, Coordination Chem. Revs., 3, 319 (1968)

26 L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, Wiley-Interscience, London, (1969)

27 J. Chatt and M.L. Searle, Inorg. Synth., 5, 210 (1957)

28 W.H. Bradley and L.M. Venanzi, Inorg. Chem., 5, 33 (1960)

29 G. Wilke, H. Schott and P. Heimbach, Angew. Chem. Int. Ed. (Engl), 6, 92 (1967)

30 R.S. Nyholm and P. Royo, Chem. Comm., 421 (1969)

31 L. Wöhler, K. Ewald and H.G. Kral, Ber., 66, 1638 (1933)

32 J.K. Stille and K.S.Y. Lau, Accts. Chem. Res., 10, 434 (1977)

33 F.R. Hartley, Organometallic Chem. Revs., A, 6, 119 (1970)

34 J. Chatt and L.M. Venanzi, J. Chem. Soc., 3858 (1955): idem ibid 2445 (1957)

35 A.C. Smithies, M. Rycheck and M. Orchin, J. Organometallic Chem., 12, 199 (1965)

36 G.M. Badley, J. Chatt, R.L. Richards and G.A. Sim, Chem. Comm., 1322 (1969)

37 G. Calvin and G.E. Coates, J. Chem. Soc., 2008 (1960)

38 S.J. Ashcroft and C.T. Mortimer, J. Chem. Soc. A, 930 (1967)

39 H.C. Clark, P.W.R. Corfield, K.R. Dixon and J.A. Ibers, J. Amer. Chem. Soc., 89, 3360 (1967)

40 E.M. Badley, J. Chatt and R.L. Richards, J. Chem. Soc. A, 21 (1971)

41 A. Del Pra, G. Zanotti, G. Bombieri and R. Ros, Inorg. Chim. Acta., 36, 121 (1979)

42 R.P. Stewart and P.M. Treichel, J. Amer. Chem. Soc., 2710 (1970)

43 F.R. Hartley, Chem. Revs., 69, 799 (1969)

44 J. Chatt and L.M. Duncanson, J. Chem. Soc., 2939 (1953)

45 J.A. Wunderlich and D.P. Mellor, Acta Cryst, 7, 130 (1954): idem ibid 8, 57 (1955)

46 S. Maricic, C.R. Redpath and J.A.S. Smith, J. Chem. Soc., 4905 (1963)

47 G.R. Davies, W.H. Hewerston, R.H.B. Mais and P.G. Owston, Chem. Comm., 423 (1967)

48 A. Evans, C.T. Mortimer and R.T. Puddiphatt, J. Organometallic Chem., 85, 101 (1975)

49 P.J. Hendra, D.B. Powell, Spectrochim. Acta., 17, 913 (1961): C.R. Kistner, J.H. Hutchinson, J.R. Doyle and J.C. Storlie, Inorg. Chem., 2, 1255 (1963)

50 J. Chatt, L.M. Vallarino and L.M. Venanzi, J. Chem. Soc., 2496 (1957)

51 G.K. Anderson and R.J. Cross, J. Chem. Soc. Dalton, 1434 (1980)

52 M.L.H. Green and P.L.I. Nagy, Adv. Organometallic Chem., 2, 325 (1964)

53 D.F. Pollock and P.M. Maitlis, J. Organometallic Chem., 26, 407 (1971)

54 R.J. Cross and R. Wardle, J. Organometallic Chem., 23, C4 (1970)

55 J.R. Doyle, J.H. Hutchinson, N.C. Baenziger and L.W. Tresset, J. Amer. Chem. Soc., 83, 2768 (1961)

56 J.X. McDermott, J.F. White and G.M. Whitesides, J. Amer. Chem. Soc., 98, 6521 (1976)

57 P. Foley, R.D. Cosmo and G.M. Whitesides, J. Amer. Chem. Soc., 102, 6713 (1980)

58 P.M. Maitlis, Pure Appl. Chem., 33, 489 (1973: K. Mosely and P.M. Maitlis, J. Chem. Soc. Dalton, 169 (1974)

59 R.J. Al-Essa, R.J. Puddlephat, P.J. Thomson and C.F.H. Tipper, J. Amer. Chem. Soc., 102, 7546 (1980)

60 P. Keller and A. Moradpour, J. Amer. Chem. Soc., 102, 7193 (1980)

61 P.A. Grieco, T. Takagawa, S. Bongers and H. Tanaka, J. Amer. Chem. Soc., 102, 7587 (1980)

62 A. Cowell and J.K. Stille, J. Amer. Chem. Soc., 102, 4193 (1980)

63 J.T. van Gemert and P.R. Wilkinson, J. Phys. Chem., 68, 645 (1964)

64 G.P. Chiusoli, Pure Appl. Chem., 52, 635 (1980): K. Kikikawa, N. Nagira, N. Terao, F. Wada, T. Matsuda, Bull. Chem. Soc. Jap., 52, 2609 (1979)

65 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, Wiley Interscience, New York, 2nd Edition, 1967.

66 F. Basolo and R.G. Pearson, Progr. Inorg. Chem., 4, 381 (1962)

67 I.I. Chernyaev, Ann. Inst. Platine U.S.S.R., 4, 243 (1926): CA 21, 2620 (1927)

68 L. Cattalani, Prog. Inorg. Chem., 13, 263 (1970)

69 J. Chatt, L.A. Duncanson and L.M. Venanzi, J. Chem. Soc., 4456 (1955)

70 L.E. Orgel, J. Inorg. Nucl. Chem., 2, 137 (1956)

71 A. Pidcock, R.E. Richards and L.M. Venanzi, J. Chem. Soc., A, 1707 (1966)

72 T.G. Appleton, H.C. Clark, L.E. Menzar, Coord. Chem. Revs., 10, 335 (1973)

73 S.S. Zumdahl and R.S. Drago, J. Amer. Chem. Soc., 90, 6669 (1968)

74 D.A. Russell, M.A. Mazid and P.A. Tucker, J. Chem. Soc. Dalton, 1737 (1980)

75 L. Manojlovic Muir, K.W. Muir and T. Solomun, J. Organometallic Chem., 142, 265 (1977)

76 F.H. Allan and S.N. Sze, J. Chem. Soc., A, 2054 (1971)

77 R.J. Goodfellow, P.L. Goggin and D.A. Duddell, J. Chem. Soc., A, 504 (1968): D.M. Adams, J. Chatt and A.D. Westland, J. Chem. Soc., 734 (1964)

78 G.M. Bancroft and K.D. Butter, J. Amer. Chem. Soc., 96, 7208 (1974)

79 J.K. Burdett and J.A. Albright, Inorg. Chem., 18, 2112 (1979)

80 D.R. Armstrong, R. Fortune and P.G. Perkins, Inorg. Chim. Acta., 9, 9 (1974): idem ibid 17, 73 (1976)

81 P. Haake and R.M. Pfeiffer, Chem. Com., 1330 (1969): idem J. Amer. Chem. Soc. Chem. Comm., 92, 4996 (1970): idem ibid, 92, 5243 (1970)

82 D.G. Cooper and J. Powell, J. Amer. Chem. Soc., 95, 1102 (1973): idem J. Chem. Soc. Chem. Comm., 749 (1974)

83 W.J. Louw, Inorg. Chem., 16, 2147 (1977)

84 R. Roulet, R. Favez, A.A. Pinkerton and D. Schwarzenbach, Inorg. Chem., 19, 1356 (1980)

85 G.K. Anderson and R.J. Cross, Chem. Soc. Rev., 9, 185 (1980)

86 G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, J. Chem. Soc. A, 1877 (1971): R. Romeo, D. Miniti and M. Trozzi, Inorg. Chem. Acta., L15, 14 (1975): idem. Inorg. Chem., 15, 1134 (1975): R. Romeo, ibid 17, 2040 (1978)

87 R. van Eldik, D.A. Palmer and J. Kelm, Inorg. Chem., 18, 572 (1979): R. van Eldik, H. Kelm and W.J. Louw, ibid 19, 843 (1980): idem ibid 19, 2878 (1980)

88 C.A. Tolmon, Chem. Revs., 77, 313 (1977)

89 P. Fitton, M.D. Johnstone and J. McKeon, Chem. Comm., 6 (1968)

90 L. Vaska, Accts. Chem. Res., 1, 335 (1968): idem. J. Amer. Chem. Soc., 93, 6671 (1971): L. Vaska and L.S. Chen, Chem. Comm., 1080 (1971)

91 I.M. Blacklaws, L.C. Brown, E.A.V. Ebsworth and F.J.S. Reed, J. Chem. Soc. Dalton, 877 (1978)

92 J. Kuyper, Inorg. Chem., 16, 2171 (1977): idem ibid, 17, 77 (1978)

93 P.B. Chock and J. Halpern, J. Amer. Chem. Soc., 88, 3511 (1966)

94 R.G. Pearson and W.R. Muir, J. Amer. Chem. Soc., 92, 5519 (1970)

95 J.S. Bradley, D.E. Connor, D. Dolphin, J.A. Labinger and J.A. Osborn, J. Amer. Chem. Soc., 94, 4043 (1972)

96 J.K. Jawad and R.J. Puddephat, Chem. Comm., 873 (1974)

97 T.G. Appleton, L.E. Menzer and H.C. Clark, J. Organometallic Chem., 65, 275 (1974)

98 P.S. Braterman, R.J. Cross and G.B. Young, J. Chem. Soc. Dalton, 1892 (1977)

99 H.A. Brune and J. Ertl, Leibigs. Ann. Chem., 928 (1980)

100 G.M. Whitesides, J.F. Gaasch and E.R. Stredonsky, J. Amer. Chem. Soc., 94, 5258 (1972)

101 R.R. Schrock, J. Amer. Chem. Soc., 96, 6796 (1974)

102 D.J. Cardin, M.J. Doyle and M.F. Lappert, J. Chem. Soc. Chem. Comm., 927 (1972)

103 A.A. Kiffen, C. Masters and L. Raynand, J. Chem, Soc. Dalton, 853 (1975)

104 A.J. Cheney, B.J. Mann, B.L. Shaw and R.L. Slade, Chem. Comm., 1176 (1970)

105 G.W. Parshall, Accts. Chem. Res., 3, 139 (1970)

106 M.A. Bennet and D.L. Miller, J. Amer. Chem. Soc., 91, 6983 (1969)

107 W. Keim, J. Organometallic Chem., 14, 179 (1968): idem ibid, 19, 161 (1969)

108 F. Hartley, Angew. Chem. Int. Ed. (Engl.), 11, 596 (1972): E. Forsellini, C. Bombieri, B. Crociani and T. Baschi, Chem. Comm., 1203 (1970)

109 E. Linder and R. Grimmer, J. Organometallic Chem., 33, C77 (1971)

110 (i) G. Booth and J. Chatt, Proc. Chem. Soc., 67 (1961): (ii) idem J. Chem. Soc. A, 634 (1966)

111 Y. Yamamoto and H. Yamazaki, Coord. Chem. Revs., 8, 225 (1972)

112 A. Wojcicki, Adv. Organometallic Chem., 12, 31 (1974): J.D. Cotton and G.T. Crisp, J. Organometallic Chem., 186, 137 (1980)

113 M.F. Lappert and B. Prokai, Adv. Organometallic Chem., 5, 225 (1967)

114 K. Noack and F. Calderazzo, J. Organometallic Chem., 10, 101 (1967)

115 R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc., 84, 2499 (1962)

116 R.J. Cross and G.K. Anderson, J. Chem. Soc. Dalton, 712 (1980)

117 S. Otsuka, A. Nakamura and T. Yoshida, J. Amer. Chem. Soc., 91, 7178 (1969)

118 Y. Yamamoto and H. Yamazaki, Bull. Chem. Soc. Jap., 43, 3634 (1970): idem ibid 43, 2653 (1970)

119 H. des Abbeys and A. Buloup, J. Chem. Soc. Chem. Comm., 1090 (1978)

120 Y. Yamamoto and H. Yamazaki, Inorg. Chem., 13, 438 (1974)

121 H.Berke and R. Hoffman, J. Amer. Chem. Soc., 100, 7224 (1978)

122 R.G. Pearson and M.M. Muir, J. Amer. Chem. Soc., 88, 2163 (1966)

123 F. Basolo, H.B. Gray and R.G. Pearson, J. Amer. Chem. Soc., 82, 4200 (1960)

124 J. Chatt and B.T. Heaton, J. Chem. Soc. A, 2745 (1968): J. Chatt and J.M. Davidson, J. Chem. Soc., 2433 (1964)

125 R.G. Hayter and S.F. Humiec, Inorg. Chem., 2, 306 (1963)

126 G.W. Bushnell, K.R. Dixon, R.G. Hunter and J.J. McFarland, Canad. J. Chem., 50, 3694 (1972)

127 M.M. Muir and E.M. Canzio, Inorg. Chim. Acta., 4, 565, 568 (1970)

128 J.E. Teggins, D.R. Gano, M.A. Tucker and D.S. Martin, Inorg. Chem., 6, 69 (1967): J.E. Teggins and D.S. Martin ibid, 6, 1003 (1967)

129 H. Motschi, P.S. Pregasin and L.M. Venanzi, Helv. Chim. Acta., 62, 667 (1979)

130 M.K. Cooper, P.J. Guerney and M.McPartlin, J. Chem. Soc. Dalton, 349 (1980)

131 G.K. Anderson, R.J. Cross, L. Manjlovic-Muir, K.W. Muir and T. Solomun, J. Organometallic Chem., 170, 385 (1979)

132 J. Chatt, J. Chem. Soc., 652 (1951): C. Eaborn, K.J. Odell and A. Pidcock, J. Chem. Soc. Dalton, 1288 (1978)

133 S.E. Livingstone and A. Whitley, Austra. J. Chem., 15, 175 (1962)

134 J. Powell and T. Jack, Inorg. Chem., 11, 1039 (1972)

135 (i) R.G. Goodfellow, Chem. Comm., 114 (1968): (ii) W. McFarlane, J. Chem. Soc. Dalton, 324 (1974): (iii) D.A. Redfield and J.H. Nelson, J. Amer. Chem. Soc., 96, 6219 (1974): (iv) A.W. Verstuyft and J.H. Nelson, Synth. React. Inorg. Metal-Org. Chem., 5, 69 (1975):

(v) A.W. Verstuyft, D.A. Redfield, L.W. Cary and J.H. Nelson, Inorg. Chem., 15, 1128 (1976)

136 J.M. Coronas, G. Muller, M. Rocamora and J. Sales, J. Organometallic Chem., 184, 263 (1980)

137 J.R. Briggs, C. Crocker, W.S. McDonald and B.L. Shaw, J. Organometallic Chem., 181, 213 (1979): idem. J. Chem. Soc. Dalton, 64 (1980)

138 R.J. Goodfellow, P.L. Goggin and D.A. Duddell, J. Chem. Soc. A., 504 (1968)

139 E.A.V. Ebsworth, B.J.L. Henner and F.J.S. Reed, J. Chem. Soc. Dalton, 272 (1978)

140 F.H. Allan and A. Pidcock, J. Chem. Soc. (A), 6, 2700 (1068)

141 S.O. Grimm, R.L. Keiter and W. McFarlane, Inorg. Chem., 6, 1133 (1967)

142 G.G. Mather, A. Pidcock and G.J.N. Rapsey, J. Chem. Soc. Dalton, 2095 (1973)

143 J. Chatt and R.G. Wilkins, J. Chem. Soc., 525 (1956) and references therein

144 G.K. Anderson and R.J. Cross, J. Chem. Soc. Dalton, 1988 (1980)

145 A.J. McLennan and R.J. Cross, Univ. of Glasgow, personal communication

146 J.A. Davies, F.R. Hartley and S.G. Murray, Inorg. Chem., 19, 2299 (1980)

147 L. Maier, Organic Phosphorus Compounds, vol. 4, Ch.7, p.1, J. Wiley & Sons, New York, 1972

148 P.M. Treichel and R.W. Hess, J. Amer. Chem. Soc., 92, 4731 (1970): P.M. Treichel and K.P. Wagner, J. Organometallic Chem., 61, 415 (1973)

149 G.A. Larkin, R. Mason and M.G.H. Wallbridge, J. Chem. Soc. Dalton, 2305 (1975)

150 R.L. Richards, Inorg. Synth., 19, 174 (1974)

151 M.J. Church and M.J. Mays, J. Chem. Soc. (A), 3074 (1968)

152 P.M. Treichel, W.J. Knebel and R.W. Hess, J. Amer. Chem. Soc., 93, 5424 (1971)

153 L. Chugaev, Compt. Rend., 159, 188 (1914): L. Chugaev and P. Teearu, Chem. Ber., 47, 568 (1914)

154 K. Hofmann and G. Bugge, Chem. Ber., 40, 1772 (1907): L. Ramberg, Chem. Ber., 40, 2578 (1907)

155 M. Gautier, Ann. Chim. et Phys. [IV], 17, 203, 222 (1869)

156 W.A. Hofmann, Ann. Chem. et Phys. [IV], 17, 210 (1869): idem Annalen, 144, 117 (1867)

157 I.K. Ugi and R. Meyer, Angew. Chem., 70, 702 (1958)

158 T. Mukuyama, H. Nambu and M.O. Kamoto, J. Organic. Chem., 27, 3615 (1962)

159 G.F. van Hecke and W.D. Horrocks Jr., Inorg. Chem., 5, 1960 (1966)

160 J. Browning, P.L. Goggin and R.J. Goodfellow, J. Chem. Res., M4201, S328 (1978)

161 E.K. Anderson and R.J. Cross, J. Chem. Soc. Chem. Comm., 819 (1978)

162 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20, 944 (1981)

163 L. Manjlovic Muir, K.W. Muir and A. Frew, Univ. of Glasgow, personal communication

164 G.W. Gokel, I.K. Ugi and W.P. Weber, Angew. Chem. Int. Ed. (Engl.), 11, 530 (1972)

165 R.W. Glyde and R.J. Mawby, Inorg. Chem., 10, 854 (1971)

166 M. Green, R.J. Mawby and C.J. Wilson, J. Chem. Soc. Dalton, 422 and 1293 (1974)

167 R. Zanella, G. Carturan, M. Graziani and U. Belluco, J. Organometallic Chem., 65, 417 (1974)

168 P.E. Garrou and R.F. Heck, J. Amer. Chem. Soc., 98, 4115 (1976): J.V. Minkiewicz and R.F. Heck, Inorg. Chem., 17, 2809 (1976)

169 P.S. Pregosin, R. Favez, R. Roulet, T. Boschi, A. Michelin and R. Roz, Inorg. Chim. Acta., 45, L7 (1980)

170 M. Kuboto, R.K. Rothrock and J. Geibel, J. Chem. Soc. Dalton, 1267 (1973)

171 A. Dormand and A. Dahchour, J. Organometallic Chem., 193, 321 (1980)

172 H.C. Clark and L.E. Menzer, Inorg. Chem., 11, 503 (1972): T.G. Appleton H.C. Clark and R.J. Puddephat, ibid 11, 2074 (1974)

173 G.B. Young, Ph.D. Thesis, University of Glasgow, 1975

174 J.F. Nixon and A. Pidcock, Ann. Rev. NMR Spec., 2, 345 (1969)

175 W. McFarlane, J. Chem. Soc. Dalton, 324 (1974): idem, Quart. Rev., 23, 187 (1969)

176 U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press, 1974

177 B.L. Shaw, B.G. Mann, C. Masters, R.M. Slade and R.E. Stainbank, Inorg. Nucl. Chem. Lett., 7, 881, (1971)

178 G.K. Anderson, R.J. Cross, Univ. of Glasgow, personal communication

179 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20, 1636 (1981)

180 A. Mantovani, G. Fachin, T. Baschi and B. Crociani, J. Organometallic Chem., 206, C11 (1981)

181 O.J. Scherer and H. Jungmann, J. Organometallic Chem., 208, 153 (1981)

182 C. Eaborn, K. Kundu and A. Pidcock, J. Chem. Soc. Dalton, 933 (1981)